A TREATISE ON

COLOUR MANUFACTURE

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A TREATISE ON
COLOUR MANUFACTURE

A GUIDE TO THE
PREPARATION, EXAMINATION, AND APPLICATION
OF ALL THE PIGMENT COLOURS IN
PRACTICAL USE

BY

GEORGE ZERR AND DR. R. RÜBENCAMP

AUTHORISED ENGLISH EDITION
BY
DR. CHARLES MAYER

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WITH NUMEROUS ILLUSTRATIONS AND TABLES

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PREFACE TO ENGLISH EDITION

THE "*Handbuch der Farbenfabrikation*" by George Zerr and Dr. R. Rübencamp at once achieved success, being recognised as a great advance on anything previously published on this subject.

There being no English work on Colour Manufacture approaching it in the fulness of its scope, the completeness of its details and its treatment of modern practice, arrangements were made with the enterprising Publishers, Messrs. Charles Griffin and Co., Ltd. (whose standard Manuals on Colour Manufacture by the late Geo. H. Hurst are so well known), to issue an English edition, and I am indebted to them for the careful oversight of my translation.

My experience of English practice has led me to omit certain portions of the German text which I judged to be of comparatively small value to English readers, and, on the other hand, I have added notes necessitated by recent developments in Colour Manufacture, some of which are based on my own practice.

CHARLES MAYER.

BURGDORF (SWITZERLAND)
July 1908.

ADDENDA

PAGE 141, LINE 6.—Pale lemon chromes can also be produced without sulphuric acid by direct precipitation of lead acetate with a solution of potassium bichromate, partly neutralised with soda. The solution must be very dilute, and be used at 3° to 4° C. These chromes are very soft, of very low specific gravity, and are of a greenish pale lemon shade.

PAGE 171, LINE 4.—*Oxidation with Chlorine.*—Experience proves that the oxidising medium has particularly a toning influence, while the colouring power, the specific gravity, and the depth of the shade rather depend on the strength of the solutions used and the manner and duration of boiling.

INTRODUCTION

During the last decades the colour industry has made an extraordinary advance, the extent of which may be estimated from the manufacture of lake-colours, and more especially by the increase of scientific method and technical skill brought to bear on the preparation of artificial mineral pigments.

Up to within the last quarter of a century the managers and workmen employed in the latter department were to a large extent devoid of any chemical training, whereas at the present time all the more important colour factories are controlled by chemists having a thorough practical and theoretical knowledge of the subject. It is in consequence of this change of management that the recent progress in this industry has been so rapid. At the same time there has grown up an extensive and highly technical literature, which has had an important influence in bringing about this satisfactory advance.

As the current technical literature is constantly pouring forth an enormous supply of fresh material with no apparent system, since each branch of the industry has its own special periodicals, there is an immediate need for a manual dealing with the colour industry as a whole. It should work up the accumulated material in a comprehensive and systematic way, eliminate what is superfluous and obsolete, supplement and bring up to date that which is old, and thereby serve as a standard reference book for the colour industry.

On the one hand, such a manual should serve as a work of reference to the chemist, whence he can get useful advice, whether he be a novice or already has some practical experience. On the other hand, the manual should fulfil the requirements of those who, whilst acquainted with the practical side of colour-making, possess at the most only a little theoretical experience, as well as the needs of merchants engaged in the colour trade; and the information it affords should be given in a readily comprehensible manner. Moreover, in consequence of the different applications of the pigment colours to technical purposes, the number of customers is naturally very large. Furthermore, seeing that a successful and advantageous use of colours is dependent on a thorough knowledge of their qualities, the authors are faced by the additional task of giving advice to the various users, so as to simplify and facilitate their work.

In consequence, this manual is primarily intended to meet the requirements of practice. It does not lay claim to be a perfect compendium of colour manufacture; it does not mention all the innumerable patents connected with the industry, or specify all the proposals and experiments made by colour chemists for the purpose of simplifying and improving the processes of manufacture.

By abandoning these pretensions a deal of matter that has no practical value is avoided. On the other hand, the materials utilised in practice and the methods actually employed will be treated with sufficient fulness to enable the technical reader or those desiring to become acquainted with colour-making to find useful information and reliable advice.

The manufacture of colours is one of the oldest branches of industry about which documentary evidence exists, the use of colours being of great antiquity, and copious evidence is available in the form of old works of art and architectural monuments respecting the use of colours in historical and prehistoric times. That the ancients not only understood colour-making, but also the process of dyeing, is proved by old Egyptian wall pictures representing human figures clad in coloured garments. Besides the Egyptians, the Chinese, Phœnicians, and Greeks paid attention to colour-making even in the earliest ages known; and during the course of many centuries continued progress was made. Subsequently the attempts of the alchemists in connection with the production of gold were greatly beneficial, directly and indirectly, to the colour-making industry: directly by the discovery of a whole series of compounds in the course of experiments with metals and mineral substances, which compounds have proved highly useful as pigments, some of them being still in use for that purpose; indirectly because the efforts and activity of these workers laid the foundation of the science of chemistry, on which the modern colour industry is based.

Up to the discovery of America the dyeing and colour-making industries were chiefly carried on by Italians. Subsequently the Spaniards, Portuguese, and Dutch held the predominant place in the commerce of the world; but though consequently the art of dyeing was more extensively practised, it made little if any progress in France, England, and Germany. The reason for this was that the guilds existing in these countries would only allow their members to use certain native dyeing materials, and restricted them to certain processes. Political motives also intervened, such, for instance, as the prohibition of the use of indigo and logwood in England, Germany (by the Imperial Diet at Regensburg in 1594), and France (1609), though certainly that policy protected the cultivation of woad in the countries in question.

The first comprehensive work on the art of dyeing appeared in England in 1605, and this work dealt with nearly all the materials then known—namely, woad, indigo, madder, alder-bark, safflower, broom, gallnuts, orchil, kermes, logwood, fustic, Brazil-wood, cochineal, &c. The eighteenth and nineteenth centuries witnessed unexpected developments in this industry. In 1690 the Dutch chemist Drebbel published a practical method of preparing cochineal. Diesbach, of Berlin, first produced Prussian blue in 1704. Scheele in 1742–86 prepared the green copper pigment bearing his name (Scheele's green). In 1826 Guimet, of Lyons, made artificial ultramarine, but kept the process secret, while Gmelin in 1828 gave directions for the technical preparation of this substance.

The oldest of all organic dye-stuffs is picric acid. In 1845 Guinon recommended this product (which was already known) for dyeing purposes, Picric acid is an oxidation product of phenol which is derived from coal tar. Already in 1835 Runge had discovered aniline also in coal tar. Later on Bröner discovered benzol, and thus gave the initial impulse to the enormously important coal-tar colour industry, founded in 1856 by Perkins' discovery of mauveine.

A great number of chemical compounds possessing definite characteristic colours are known, these colours for the most part only appearing when the compounds are formed, and disappearing when they are decomposed. It frequently happens that one or more of the components forming these compounds have an entirely different colour from that of the finished compounds. Thus the combination of mercury and sulphur, for instance, furnishes the beautiful red pigment vermilion, although neither of the original elements is of that colour. Similarly, the well-known ultramarine blue is produced from ingredients none of which is of that colour. Some ingredients of colouring matters, however, already possess to some extent the colour of the finished product resulting from their combination; for instance, the reddish tint of the chromate of potash from which orange chrome is made, the blue colour of the copperas used in the production of Bremen blue, &c. Experience shows that such characteristically coloured compounds cannot be produced in the same state of combination without exhibiting their special colour, neither can their colouring substance be isolated; they must therefore be regarded as substantive colours.

These substantive colours may be mixed in any proportion with "white" materials—*i.e.*, colourless in a scientific sense—to which they impart their own tint, forming a colouring matter from which the pigment can again be isolated.

Most of the natural pigments used for technical purposes and called "natural mineral colours" belong to this category. These colours essentially consist of colourless salts, and owe their appearance more or less to admixtures of iron, manganese, copper, or chromium compounds, the latter being therefore colouring matters in the true sense of the term. Conversely, it is incorrect to speak of "colouring matter" in the case of the *pure* natural and artificial mineral colours, these being chemical compounds in which the colour is a special inherent property.

Artificial mineral colours are those it has been found possible to manufacture in imitation of the corresponding natural products. Progress in chemical analysis has enabled the elements composing the natural mineral colours to be detected; their artificial production followed as the next step in advance; and in this way many natural mineral colours formerly very rare, and therefore very expensive, can now be cheaply produced in unlimited quantities, of purer condition and of a far more brilliant tint—for example, ultramarine blue, Bremen blue, &c. Such pigments—for instance, chrome yellow, Paris blue—as do not exist in nature have been placed in the same class as the artificial mineral colours.

In order to treat a subject in a thoroughly scientific and technical way it is necessary to proceed on systematic lines; but in endeavouring to arrive at a systematic classification of colouring matters great difficulties are encountered. In most cases the connection and relations between the chemical and physical properties prevent any hard and fast line of demarcation being drawn. Nor can any satisfactory system be established on the basis of chemical structure or shade of colour. Hence, in the first place, it is preferable to divide these substances into two chief classes, viz.:

I. The natural inorganic and organic colours.
II. The artificial colours.

Natural colours are those found in nature in a finished state and generally obtained by mining. The question is therefore one about minerals, and we have to deal essentially with the wide subject of the so-called earth colours. Some other inorganic colours, such as vermilion, lapis lazuli, &c., have almost gone out of use, their place being taken by the corresponding artificial products, which are better adapted for technical use.

The **natural organic colours** are met with in the vegetable and animal world, some being in the finished state (cochineal, purple snail, sepia), whilst others (indigo, madder) need preparation.

The **artificial colours** are subdivided into the inorganic and organic groups.

The **inorganic pigments** result from chemical transformations—viz., the formation of salts, the oxidation of metals, &c. The **organic colours** are obtained by complex chemical processes from a number of definite compounds, which are isolated from the distillation products of coal, and recently, in some cases, from peat and petroleum. Those colouring matters, too, are really indirectly derived from vegetable or animal substances, whose fossilised remains form the raw materials for the manufacturing processes.

By adopting this system the entire series of pigments can be classified into the proper subdivisions.

In the first place it is necessary to explain the term "salt" in its chemical sense, since in the manufacture of chemical pigment colours we have to deal solely with simple transformations of saline substances, prepared for the most part by easy methods, and almost exclusively employed for this purpose in the state of aqueous solutions.

A *salt* is the product arising from the combination of a base with an acid.

The term *acid* is generally understood in practice, whereas the meaning of the word *base* is less frequently comprehended.

All elements enter into combination with hydrogen and oxygen, the resulting compounds being termed oxides if oxygen alone has entered into combination, and hydroxides if both hydrogen and oxygen are concerned in forming the product. Many of these hydroxides, and primarily those of all non-metallic elements, exhibit a sour taste and possess the property of dyeing litmus-paper red, thus proving themselves to be acids. Another property to be considered is their faculty of exchanging their combined hydrogen for a metal when they are allowed to react on metallic oxides. In such case the metallic oxide or hydroxide acts as a base.

"Bases" are elements or compounds with properties antithetical to acids, and reacting with them to form compounds termed *salts*, in which the acid or basic properties are more or less lost, but which are themselves neither acids nor bases.

By treating metallic zinc with sulphuric acid a certain proportion of the metal is dissolved. The new compound formed has neither the character of zinc nor that of sulphuric acid, but represents a salt—sulphate of zinc—exhibiting perfectly definite properties peculiar to itself. The same compound can also be obtained by treating zinc white, a combination of metallic zinc and oxygen (zinc oxide), in a similar way with sulphuric acid. In these reactions the metallic zinc and the zinc oxide act as bases. Metals and all analogous substances, as well as compounds, play the part of bases.

Salts are divided into:

1. Neutral salts.
2. Acid salts.
3. Basic salts.

Neutral salts are those in which the whole of the displaceable hydrogen of the acid has been replaced by a metal.

Acid salts are those in which only part of this hydrogen has been displaced by metals. They are still able in many cases to act like acids. In the *basic salts*, however, the character of a base still predominates, and in fact they continue to exhibit a partially basic reaction. They therefore behave in relation to their bases in the same manner as the acid salts do to their acids. Hence the basic salts may be regarded as compounds of neutral salts with the same unsaturated base as is present in a saturated condition in the salt.

In addition to these three kinds of salts, there is another particular class, the so-called *double salts*, in which the hydrogen in acids containing more than one atom of displaceable hydrogen has been replaced by a plurality of bases. In giving the definition of salts mention has already been made of chemical compounds, and experience shows that the terms "combination" and "mixture" are very often confused. When fine iron filings are mixed with flowers of sulphur a powder is obtained which has no external resemblance to its constituents, and might therefore be considered as quite a new body This opinion, however, would be quite wrong, the product being only a *mixture*, both the elements of which have retained their properties. With the magnifying glass it can be readily seen that the iron and sulphur are still unchanged. On heating this mixture the whole mass suddenly takes fire—a sign of incipient chemical combination; and when the whole is cooled down we have a product with entirely different properties. In the first place the mass no longer reveals particles of "iron" or "sulphur" under the microscope, and the fragments of iron cannot now be separated from the mixture by the aid of a magnet as they could before. The new and entirely changed substance obtained by heating the mixture of iron and sulphur is what is called a *chemical compound* of sulphur and iron.

Chemical compounds are only formed by the mutual reaction of substances when in the most intimate contact obtainable either by pulverisation, fusion, or solution. The latter process is the one principally used in the manufacture of pigment colours.

The chemical combination of two or more elements only occurs in well-defined proportions by weight, these being unalterable and capable of expression in figures. These figures, which express the relative quantities (by weight) of the elements that enter into combination with others, may be called the *combining weights of the elements.*

To simplify matters, a symbol has been given to each element, *i.e.*, a definite abbreviated sign, consisting for the most part of the initial letter of its Latin name.

Table I. (see Appendix) contains the most important elements, with their symbols and atomic weights. The chief elements used in colour-making are marked *. Table I. also contains the coefficients expressing the valency or combining power of the different atoms in their saturated combinations with hydrogen. This valency is denoted by Roman numerals. It is therefore seen that certain elements are able to combine with more than one atom of hydrogen (regarded as the standard monovalent atom), some of them being able to combine with four atoms of hydrogen, or two atoms of a divalent element. Take, for instance, the following combinations: Chlorine and hydrogen are both monovalent, and therefore we get the compound $HCl =$ hydrochloric acid. Oxygen is divalent, and furnishes the compound $H_2O =$ water. Nitrogen, as a trivalent element, gives the compound $NH_3 =$ ammonia; and from the tetravalent element carbon the compound CH_4 = methane can be formed. The divalent body sulphur combines with divalent iron and forms FeS = sulphide of iron. It must be remembered, however, that one and the same element may appear with a different valency in different combinations.

The practical importance of the figures given in Table I. may be made clearer by an example. When melting iron filings with sulphur we should take, in order to obtain the exact equivalent proportions of the combining weights, 56 parts of filings and 32 parts of sulphur (according to Table I.), so as to avoid a surplus of the one or the other element. Otherwise the whole would not enter into combination, and part of the material would be superfluous. The proportion of $56:32$ can be, of course, diminished or increased at will; *e.g.*, $28:16 = 14:8 = 7:4 = 21:12$, &c.

Water is used as a general agent for dissolving or diluting solid and liquid materials, salts, acids, and bases, the temperature employed for the operation being an important factor. As a rule bodies dissolve more readily at a higher temperature than they do at a lower one in the same quantity of water, but there are exceptions to this rule. Glauber salt (crystallised sodium sulphate), for instance, is less soluble in hot water than in cold, whilst the solubility of sodium chloride at a low temperature is about the same as at a high temperature.

A *saturated solution* is one which does not take up any more substance at the temperature at which the operation has been performed. A distinction must be drawn between hot- and cold-saturated solutions; for whilst a cold-saturated solution is often able to take up considerably larger quantities of the substance at a higher temperature, hot-saturated solutions, as a rule, deposit a part of the dissolved salts, in the form of crystals, when cooled.

It follows, therefore, that the solubility of each salt in water is a fixed quantity; and since, in the case of most of the chemical colours, the concentration of the solutions from which the salts are precipitated is very important, we append a table giving the exact degree of solubility of all the salts chiefly used in colour making (Table II.). At the same time this table gives the scientific and, where possible, the trade name of all raw materials used for colour manufacturing, as well as their chemical formulæ and molecular weights.

The employment of the aforesaid symbols for the chemical elements is of value, inasmuch as the combinations of the elements can be accurately expressed by suitably arranging the symbols in juxtaposition. In Table I. we find, for instance, Fe (ferrum) as the symbol for iron, and S for sulphur, By putting these two signs together we are able to express the previously mentioned combination of these two elements in the form of a symbol: FeS.

At the same time the symbols of the elements and compounds are used to denote their combining weights. The symbol Fe signifies not only the element iron, but also 56 parts by weight of iron. $O = 16$ parts of oxygen, $S = 32$ parts of sulphur, &c. To denote multiples of the combining weight of any element, we put the corresponding figure in front of or behind the symbol, $2Fe = Fe_2$, for instance, indicating 2×56 parts by weight of this element. To avoid any mistake, however, the figures in question are always put behind the symbol in the case of elements, the index being then understood as applying solely to the element in question, whilst in the case of compounds the coefficient is placed in front of the symbol, thus affecting all the elements in such compounds.

The foregoing may best be illustrated by the following example. In Table II. we find amongst the compounds of iron (to keep to this element) that oxide of iron is indicated by the formula Fe_2O_3. The molecular weight of this compound is therefore $Fe_2 = 2 \times 56 + O_3 = 3 \times 16$, or $112 + 48 = 160$. To denote a certain multiple of combining weights of oxide of iron (say 3), we must, in accordance with the above-mentioned rule, write $3Fe_2O_3$, or 3×160 (the combining weight) $= 480$ parts by weight of oxide of iron. In more complex compounds it is usual to simplify the matter by using parentheses. For instance, 3 multiples of the combining weight of crystallised copper sulphate are expressed as $3(CuSO_4 + 5H_2O)$; or 3 multiples of the combining weight of potash alum, $3(K_2SO_4 + Al_2(SO_4)_3 + 24Aq.)$.

To find the combining weight of $CuSO_4 + 5H_2O$ according to Table I., it must be calculated as follows:

$$\left.\begin{array}{lcr} Cu = & & 63 \\ S \;= & & 32 \\ O_4 = 4 \times 16 = & & 64 \end{array}\right\} + 5 \begin{array}{l} H_2 = \;\; 1 \times 2 \times 5 = 10 \\ O \;= 16 \times 5 \qquad\;\; = 80 \end{array}$$

$$\overline{159} + \qquad\qquad \overline{90} = 249 \text{ parts by weight.}$$

It has been stated that the elements combine only in the proportion of their combining weights or multiples of the same. This fact can be accounted for clearly by supposing the elements to consist of infinitely small and indivisible particles called *atoms*. One or more atoms of the one element join together with one or more atoms of another element. The proportion of the atomic weights of different elements entering in combination will be indicated by the combining weights or their multiple; therefore the combining weights are called also *atomic weights* of the elements.

The corresponding weight of a compound, being, as we have seen, the sum of the combining weights of the several components, is called the molecular weight, and the term *molecule* implies the smallest chemically indivisible quantity of a compound that can exist as such. Therefore a molecule of common salt, NaCl, consists of one atom of sodium and one atom of chlorine, and this molecule cannot be divided without ceasing to be common salt. The foregoing will suffice to explain Tables I. and II., and facilitate their practical application to technical calculations.

The process set up by the calcination of the mixture of iron filings and sulphur can be represented by the following chemical equation:

$$\underbrace{\text{Fe}}_{\text{Iron}} + \underbrace{\text{S}}_{\text{Sulphur}} = \underbrace{\text{FeS}}_{\text{Sulphide of iron}}$$
$$56 + 32 = 88 \text{ parts by weight.}$$

When red mercuric oxide is heated to redness it is split up into its constituent parts—viz., metallic mercury and oxygen. The chemical formula indicating this process is:

$$\underbrace{\text{HgO}}_{\text{Mercuric oxide}} = \underbrace{\text{Hg}}_{\text{1 atom of mercury}} + \underbrace{\text{O}}_{\text{1 atom of oxygen}}$$
$$216 \text{ parts by weight} = 200 + 16.$$

Since a chemical equation may be considered as an algebraical one, and, therefore, the sum of the combining weights on the one side must be exactly equal to the sum of the combining or atomic weights on the other side of the equation, it is easy to calculate unknown members of the equation.

Example 1.—How many grammes of mercury are to be obtained from 100 grms. mercuric oxide on decomposition at red heat?

Answer.—216 parts by weight of mercuric oxide will furnish 200 parts by weight of mercury, in accordance with the above-mentioned equation. Consequently,

$$216 : 200 = 100 : x$$
$$x = (200 \times 100) \div 216 = 92 \text{ grms.}$$

Example 2.—How many grammes of sulphide of iron can be produced from 100 grms. of sulphur?

Answer.—According to the equation, 32 parts by weight of sulphur yield 88 parts by weight of sulphide of iron. Therefore 100 grms. sulphur will give:

$$32 : 88 = 100 : x$$
$$x = (88 \times 100) \div 32 = 275 \text{ grms.}$$

In stating the definition of salts the example of metallic zinc dissolved in sulphuric acid was given. The chemical process then occurring is explained by the following equation:

$$\underbrace{\text{Zn}}_{\text{Zinc}} + \underbrace{\text{H}_2\text{SO}_4}_{\text{Sulphuric acid}} = \underbrace{\text{ZnSO}_4}_{\text{Sulphate of zinc}} + \underbrace{2\text{H}}_{\text{Hydrogen}}$$
$$65{\cdot}4 + 98 = 161 + 2 \text{ parts by weight.}$$

On considering the above equation thoroughly it will be seen that the H_2 of the sulphuric acid has been displaced by the zinc to produce the salt $ZnSO_4$, whilst the hydrogen escapes in the form of gas. This process illustrates distinctly the previous explanation of the formation of salts.

From the foregoing equation it is possible to calculate exactly the quantity of sulphuric acid required for converting a given quantity of metallic zinc into sulphate of zinc, or, conversely, the quantity of zinc needed to furnish the same result with a given quantity of sulphuric acid.

To show the importance of these calculations we will take an example from practical colour-making. Barium sulphate (*blanc fixe*) can be made by precipitating a solution of barium chloride with sulphuric acid, and the following equation represents the way in which this precipitation proceeds:

$$\underbrace{BaCl_2}_{\text{Barium chloride}} + \underbrace{H_2SO_4}_{\text{Sulphuric acid}} = \underbrace{BaSO_4}_{\text{Barium sulphate}} + \underbrace{2HCl}_{\text{Hydrochloric acid.}}$$

This equation enables the following calculations to be made:

1. The quantity of barium chloride needed with a given quantity of sulphuric acid.
2. The quantity of sulphuric acid required with an existing quantity of barium chloride.
3. The quantity of barium sulphate obtainable with a certain quantity of sulphuric acid, of barium chloride, or of the two together.
4. The quantity of free hydrochloric acid formed, and, provided the quantity of water used be known, the degree of dilution of this acid.

Commercial sulphuric acid being sold in different strengths, it is necessary in these calculations to know the percentage of pure sulphuric acid contained in the liquid used. It will be evident, of course, that more of the dilute acid must be taken to ensure complete precipitation of a given quantity of barium chloride solution of given strength than is the case with concentrated or perfectly pure acid. To simplify the occasionally rather complicated calculations a certain number of tables for the acids as well as for the saline solutions most frequently used in colour making are given at the end of the book (see Appendix).

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A.—THE ARTIFICIAL MINERAL COLOURS

PART I

GENERAL REMARKS ON THE ESTABLISHMENT OF A COLOUR WORKS

For colour works, as in all chemical factories, an ample supply of pure soft water is a very important factor, since the purity and softness of the water greatly influence the brilliance and the other qualities determining the utility and selling value of the resulting colours.

Of equal importance to the prosperity of a colour manufactory is the question how to purify and discharge the large volumes of fouled or waste water (often injurious in character), so as to satisfy legal requirements. In certain circumstances this point may become more important than the question how to obtain the water-supply, the solution of the difficulty sometimes causing endless trouble and expensive alterations. Hence the choice of situation for the establishment of a colour-works is very important, apart from the question of favourable connection with railways or other means of communication.

Hard water, containing lime, magnesia, or iron, is unsuitable for the colour manufacturer, as is also water containing more or less considerable quantities of ammonia, chlorine, nitric acid, &c., or organic bodies. River water is the best of all, being quite soft enough, and practically inexhaustible in quantity. Only the upper reaches of rivers, however, can be considered suitable, since, especially in industrial countries, the water lower down is naturally more contaminated.

In choosing the site for a colour works the possibility of an increase of business must also be taken into consideration. This circumstance, unfortunately, is usually insufficiently appreciated at the outset, if not entirely neglected. Apart from the fact that the restriction of working space may occasion great inconvenience by preventing quick delivery of orders, and thereby causing offence to customers, it has frequently happened that important firms have been forced, through lack of room for expansion, to give up their original works and build more spacious premises elsewhere at very heavy cost.

In planning a factory for manufacturing different kinds of colours care should be taken to separate the various groups, and not only provide special rooms for the manufacture of yellows, greens, blues, reds, &c., but also for the grinding, drying, and sifting processes. Although the great advantage of such an arrangement is evident, it is apparently often neglected, even in works of considerable reputation, presumably on the ground of economy. Every one engaged in colour manufacture, however, must agree that this kind of economy is a false one.

To facilitate operations and preserve the health of the work-people the workrooms should be as high as possible, bright, and well-ventilated, to ensure rapid change of air and complete removal of dust, gas, and vapours. Good ventilation is absolutely necessary in drying-rooms, where every unnecessary delay in the progress of drying means considerable loss. For drying apparatus, as a rule, air heated by direct fire is preferable to steam, on the score of economy, though it is undeniable that the former is at a disadvantage in connection with fire risk. On the other hand, whereas experience shows that steam is not suitable for all colours, especially chromes and the still more delicate chrome greens, hot air is quicker in action, and, provided perfect ventilation be employed, there is no danger of impairing the shade of the colours from overheating.* This danger arises chiefly from faulty ventilation retarding the removal of the steam given off from the colours in drying, and therefore this circumstance must be specially borne in mind in the arrangement of drying-rooms.

Many mineral colours are very liable to lose in brightness during the time consumed in the washing process. It is therefore necessary to avoid any loss of time wherever possible. A good deal of time is often lost through the supply of water being conveyed in small pipes, so that several hours are consumed in refilling a precipitating tank with water for washing. Therefore in fitting up a colour works it is very important to provide large pipes for the water-supply from the beginning, so that the necessary quantity of water can be obtained quickly and conveniently. This equally applies to steam pipes; and it should be stated that copper pipes are preferable to iron pipes, although more expensive. Iron pipes, moreover, are subject to the inconvenience of getting very rusty inside if left unused for a long time, and the rust has a bad effect on most colours when it comes into contact with the dissolved raw materials.

Wherever possible it is advisable to collect the condensed water from the steam plant and to use it for dissolving the raw materials. Owing to its purity, this water is specially adapted for dissolving coal-tar dye-stuffs, which often dissolve with difficulty in ordinary water.

The flooring of the workrooms is preferably made of asphalt or cement throughout, as such floors can be cleaned quickest and easiest and are impermeable to water. Wood, sandstone, or brick floors are unsuitable in many respects, chiefly because the materials will not stand much wear, and need frequent repairing, which makes them dearer in the long run.

The arrangement of the workrooms depends, of course, upon local considerations and the existing circumstances of each case, and therefore no definite recommendations or fixed rules can be given. Generally, however, it is advisable to arrange the available space in such a way that the rooms for wet processes are placed next the rooms containing the moulding machinery and the drying-rooms, these latter, again, being close to the rooms containing the crushing-machines, packing-room, store, and forwarding departments. Such an arrangement of the different workrooms will save much time and labour, and therefore much money as well, by the avoidance of useless and time-wasting conveyance of the goods to and fro in course of manufacture, whilst at the same time space will be economised.

---

* The temperature in drying-rooms should, as a rule, not exceed 40–50° C.

Steam is generally the best motive power for use in colour works, since the heating of the water for solution and precipitation, extracting dye woods, working high-pressure autoclaves, &c., necessitates the use of steam, this being the easiest and cheapest method of heating quantities of water or solutions quickly, since the steam also acts as a mixer and replaces stirrers. Moreover, the heating of drying-rooms and of the workrooms and offices of the establishment is most conveniently effected by steam. Therefore, since a large steam boiler must be provided in any event, the installation of a steam engine is evidently desirable for supplying motive power to the whole works. If water power be available close by (as is the case in some manufactories of earth colours and colour-mills), the steam engine need only be used for part of the premises, or at intervals, as a reserve machine. In selecting a steam boiler choice must necessarily fall on one affording a large steam space, and capable of furnishing high-pressure steam quickly, so as to supply the varying demands of the establishment at all times.

All colour factories specialise in certain lines, and therefore the different works are fitted up specially for the production of certain kinds of colour.

GENERAL PREPARATION OF THE MATERIALS

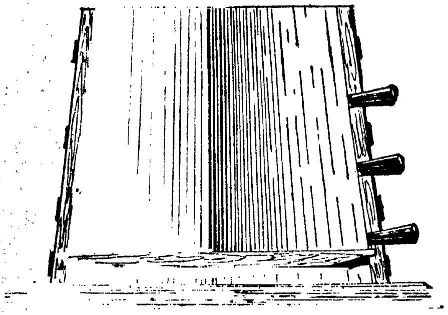
Raw Materials—Washing the Colour-Bearing Materials—Dissolving Salts—Apparatus and Machines

Preparation of Raw Materials.—The processes, apparatus, and machin used in colour-making, and described in the following chapter, can, course, only be dealt with in relation to the general manufacture and trea ment of colours. Where special arrangements of no general application a needed they will be mentioned in dealing with the colours in question.

It is not the purpose of this work to describe all the operations and inn merable (sometimes very complicated) forms of apparatus and machines used at different works in accordance with individual preferences; we will only consider such as are specially characterised by simplicity and practical value. This does not mean, however, that the operations and mechanical arrangements here described are a *sine quâ non* for obtaining satisfactory results; every manufacturer will prefer to choose his own method of working, according to his own experience and technical skill, and with regard to the special circumstances of the case. As is the case in most other branches of industry, a clever man can obtain satisfactory results in the manufacture of colours by the application of simple means.

It was stated in the Introduction that the manufacture of most colours depends on the chemical transformation of two or more salts, which for this purpose must be in the state of aqueous solution. The more dilute these solutions are employed, the finer and generally more brilliant are the resulting precipitates, and the more highly appreciated are these colours in use. Hence, in the first place, the precipitation vats used must be as large and spacious as possible. As a rule these vats (Figs. 1, 2) are very solidly made from oak or fir wood (free from knots), to hold 500–1000 gallons or more, and are provided in front with several holes at different levels, which can be tightly closed by fairly long, tapering wood plugs. These plugs are driven into the holes by means of a hammer. The arrangement of the holes is such that the lowest is placed quite close to the bottom of the tank, as shown in Fig. 2. The vat itself should be mounted upon a strong support, just high enough to enable the whole of the precipitated pasty colour to be run off into a vessel (bucket, &c.) placed underneath the hole. The best shape for these vats is decidedly the circular one, but, if rendered necessary by circumstances, square tanks with rounded corners can be used. This, however, is only advisable when the vats or tanks are always kept in the same place, since square vessels are more difficult than circular vats to tilt and move about.

FIG. 1.



In some places large oval tanks are used. In these the thorough mixing of the contents is said to be facilitated by the circumstance that the movement of the stirrers does not impart a uniform motion to the whole mass, the velocity being lower at the ends of the longer axis of the oval. On the other hand, a difficulty is caused in the case of heavy pigments by the tendency to deposition in the parts unacted on by the paddles.

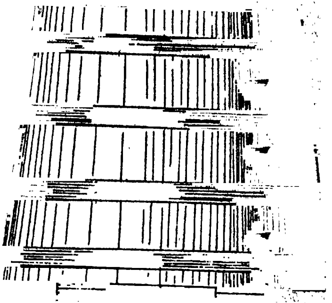
Every vat is provided with pipes for admitting cold water and steam, and it is very useful to have a supply of warm water as well.

Separate vats must be used for each kind of colour made. The method of working is generally as follows:

The solutions, prepared as will be described later on, are run into the tank, and thoroughly mixed by rapid stirring, until the conversion of the salts has been completed. The mixture being left to stand, the precipitate, which is always specifically heavier than the water, settles down to the bottom at a rate proportionate to its specific gravity and to the degree of dilution of the solutions from which it has been produced. The supernatant liquid, which is perfectly clear, and in some cases water-white, has next to be removed. This is done by drawing the plug next above the highest layer of precipitate, whereupon the liquid, which is mostly useless, runs off. After replacing the plug, the precipitate is washed by filling the vat with water and constantly stirring the mixture, the precipitate being then allowed to subside again. The same manipulation has to be repeated as described above. After some time the precipitate settles down to the bottom again, and the top liquor, now containing considerally less impurities than the first time, has in turn to be run off from the colour by drawing out the plug. This operation must be repeated as often as required for the colour in question—that is to say, until the latter is perfectly free from any admixture of impurities whatsoever.

Thoroughly efficient washing of the colours is certainly one of the most important operations in the manufacturing process. The more carefully this manipulation is performed, the greater is the certainty of obtaining a soft and loose finished dry product. This applies especially to all the colours used by lithographers, printers, &c., which, if defective, are usually so as a consequence of insufficient washing. The same cause is, in many cases, the reason why ordinary paints dry badly and imperfectly after application, because the salts still adhering to the particles of colouring matter retard the drying process, or prevent it altogether.

FIG. 2.



For stirring the liquids in the working vat use is made of suitable large and strong wooden crutches or paddles (as shown in Figs. 3 and 4), the manner in which they are used needing no further explanation. The volume of liquid being too great to be stirred efficiently by hand, mechanical stirrers are used, driven by water or steam power. In this case, however, the construction of these stirrers must be as simple as possible, since otherwise they might be rather a hindrance than an advantage in point of quickness and efficiency. The employment of specifically heavy materials, such as barytes, red lead, white lead, lead sulphate, &c., being necessary in many cases, it is inevitable that these materials, when present in such quantity as is necessary for some colours, should often settle down to the bottom so compact as to prevent the stirrers from acting without risk of breakage. Of course this danger is much greater with complicated forms of stirring apparatus. With simple apparatus, however, when such a contingency arises the whole arrangement may be taken out of the vat, and the difficulty thus easily overcome. On the other hand, when mechanical stirrers are used difficulty often arises in discharging the colours from the vat after they have settled down, and in some instances loss is inevitable. For this reason mechanical stirrers are rarely used for certain kinds; though they are generally employed for colours that are not very heavy, and therefore do not form a very dense mass in settling.

For heavy precipitates special stirring machines have been constructed, which can be lifted out after the precipitation and mixing are completed. When the top water has been run off, fresh washing water is run in, and at the same time the stirring machine is set in motion again by lowering it slowly into the vats, whereupon the conjoint action of the stirrers and the continually increasing volume of water gradually stirs up the whole of the sediment.

Fig. 5 represents a stirring device that acts well in practice, though simple, and may therefore be specially recommended here. It is made of oak throughout, and any metal fittings that cannot be dispensed with are preferably made of copper, that metal being best able to resist the action of the different salts, with a few exceptions only. Iron fittings, whether wrought or cast, should be avoided as much as possible, this metal being very detrimental to most colours.

In large works the vats are preferably erected in rows, so as to form groups of four, leaving a passage between them. The water and steam pipes are arranged in the gangway between the rows, with branch pipes and taps for each vat.

FIG. 3.

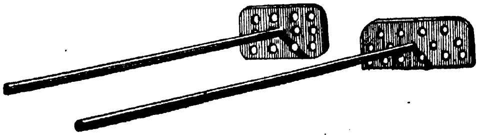
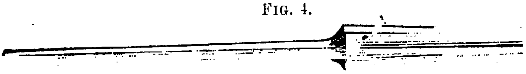


FIG. 4.

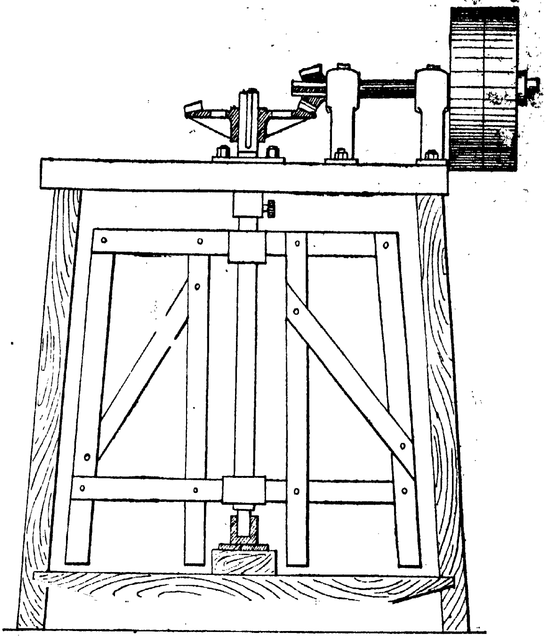


Between the pipes and the ceiling runs the shafting for driving the whole of the stirring machines, each of which can, of course, be stopped or started separately. The tanks must not stand directly on the floor, but upon a wood and iron frame, about six feet high. Underneath this frame are the filters, presses, &c., for eliminating as far as possible the water adhering to the pasty colour before drying. The supernatant liquor is drawn off by syphons, adjustably mounted on the upper edge of the vat in such a manner as to remove the clear liquid as completely as possible from the precipitate. The escaping liquor falls on to the asphalt floor, which floor, sloping toward the centre, allows the water to run away into subterranean drains. The hole for drawing off the precipitated colour is at the bottom of the vat, where a short outlet, with valve, is arranged, through which the colour paste is conveyed by means of flexible piping to the filters, filter presses, &c.

The process of dissolving the salts for colour-making is usually effected by the aid of hot or boiling water, the operation being generally too slow when cold water is used. When, however, for instance, with chromes and chrome greens, &c., cold solutions are essential, hot solutions must be diluted with cold water until the suitable temperatures have been attained. Hence, apart from the quantity of salts to be dissolved, the size of the vessels used in preparing the solutions is by no means a matter of indifference.

Where the quantities are not very large most colour-makers prefer to use petroleum barrels, with open tops or cut in two, these barrels being generally made of very strong material, well finished, and are more easily transported, on account of their very handy shape, than any other kind of vessel made of the same material. If, however, it is necessary to make large quantities at a time, it is advisable to arrange in the middle of the workroom a special system of solution vessels at a sufficient height to allow the finished solutions to be run into precipitating tanks conveniently, preferably by means of wooden gutters. Steam for heating or prolonged boiling of the solutions, and cold water for dilution, must be available in sufficient quantity. The number of vessels used for dissolving depends, of course, on the raw materials required for producing the colours; and the same vessels must be used only for such colours as are allied either by nature or method of preparation, *i.e.*, belong to the same group—for instance, the different kinds of chromes. Such colours are usually made from identical raw materials, but at different temperatures.

FIG. 5.



For reasons already referred to, the steam pipes should be made of copper, lead, or, still better, of porcelain—at least, such of them as come into direct contact with the solutions—to screw on and take off easily. The arrangement of a system of several vessels for solutions is shown in Fig. 6, and needs no further explanation.

It should be pointed out that the dissolving of certain salts in metal vessels may cause much trouble if the solution corrodes the metal. For instance, in dissolving alum in an iron vessel the solution will take up iron, and be rendered useless for colours that are injuriously affected by the presence of that metal. The same occurs with copper sulphate when dissolved in iron pans, iron then passing into solution and copper being liberated. Wooden vessels are undoubtedly the best, but where these cannot be used great care should be exercised in choosing metal vessels.

In dissolving commercial salts it should be remembered that they very often contain mechanical impurities, such as sand or particles of wood, which, of course, have not been mixed purposely, but accidentally introduced during the manufacture or packing—a circumstance which is inevitable even with the utmost care. On the other hand, some salts alter when left exposed for a long time in the open air: they effloresce, deliquesce, or oxidise. In the last event compounds are formed which are perfectly insoluble in water. Finally, it frequently happens, through the carelessness of the hands in colour works, that foreign matters find their way into the raw materials, and at the best spoil their appearance. Solutions in undistilled water sometimes turn cloudy. Water containing lime, for instance, will produce insoluble lime sulphate when used for dissolving soda sulphate; and phenomena of this kind have to be considered when they appear in any striking degree.

It is therefore necessary to filter the solutions of such impure salts before use, or to remove these impurities by sedimentation, which generally occurs to a sufficient extent when the finished solutions are left to stand for some time. To eliminate the mechanical impurities more quickly from the solution, use may be made of fine hair sieves, or bolting cloth mounted on a frame so as to form a sieve through which the solution is strained.

The vats holding the solutions must be fitted with valves or plugs close to the bottom, for drawing off the clarified liquid into the working vat. Since all vibration must be avoided in this process, the clarifying vessels must be fixed in such a position that the outlet valve is only a little higher than the edge of the precipitating tank.

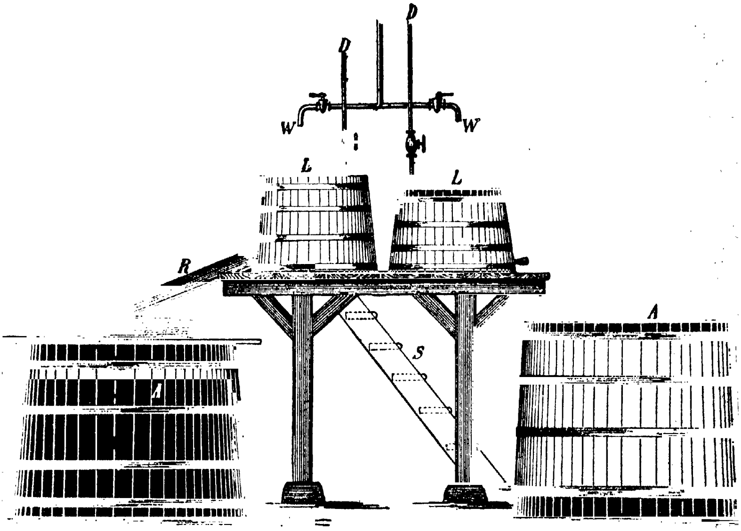
In the arrangement of the dissolving vats in Fig. 6 this circumstance has been taken into consideration, as the height of the stand whereon these vessels are fitted is only a little above that of the largest precipitating tank.

In spite of all these precautions, it is still advisable to pass the clear solution again through a fine silk, hair, or metal sieve on the way to the precipitating tank, thus preventing the passage of any impurities into the latter. This must also be done even in those cases where there is no doubt about the initial purity of the salt, since during prolonged stirring in the dissolving process impurities may possibly get into the otherwise perfectly clear solution. For instance, during prolonged stirring small fragments of wood often break off from the paddles or from the sides of the wooden dissolving tanks. The extent to which this may occur under certain circumstances is only too often revealed by a careful examination of the sediment left on the sieve by salts considered to be perfectly pure. Therefore it is advisable to use for this purpose the very finest sieves that are made. A number of these sieves should be kept, one for each different coloured solution, the square shape being preferable t the circular form,since the former can be easily made by the workmen.

For use, the sieves are laid upon a frame of two parallel smooth-planed laths, joined by cross-bars (see Fig. 7). These laths must be long enough to fit on to any of the working tanks.

The methods of dissolving the different salts, especially as regards the quantities of water to be used for this purpose, will be referred to more fully in connection with the colours in question; in this place merely some practical hints concerning the dilution of the various mineral acids used in the colour industry will be given.

Fig. 6.

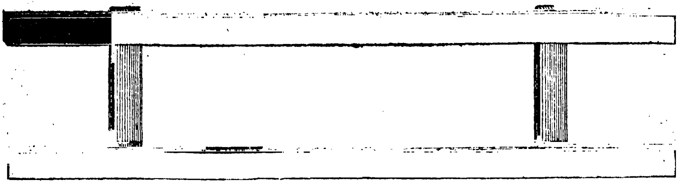


A, *A*, working vats.
L, *L*, dissolving vats.
S, stepladder.
D, *D*, steam pipes.
W, *W*, water pipe.
R, gutter or shoot.
J, sieve.

Since dilute acids, as a rule, do not attack the wood of the vessels until after a considerable lapse of time, the process of dilution can be effected, with special precautions, in wooden vats, &c., for, as a rule, the acid does not remain long in these vessels. As a rule, when diluting acids with water the latter should not be run into the acid, but, conversely, the acid should be added to the water which is already in the tank. This rule should be specially remembered when diluting concentrated sulphuric acid with water, as this operation always results in a considerable liberation of heat, the resulting temperature rising the higher in proportion as the quantity of acid in the mixture increases in relation to the quantity of water. For this reason the greatest heat is developed by pouring the water into the acid. As a matter of fact, numerous accidents have resulted from this erroneous procedure; and the frequency with which these accidents occur induces the authors to draw attention to the danger of similar imprudent methods. Furthermore, for the same reason, warm or hot water should not be used for the dilution of acids.

Compounding the Colours.—Having learned the preparation of the different solutions, the next step is the actual manufacture of the colours. This is always based on a combination of those solutions in accordance with fixed rules. The decisive factor is the order in which several solutions are employed; and this so intimately depends on the chemical composition of the colours that any departure from the rule will lead either to no result or to quite another kind of product from that expected. However, since this order varies according to the colour to be made, it will be better to give a particular description when dealing with the colours in question, and to confine ourselves at present to a reference to the general technical part of the question, in order to explain the most suitable way of mixing the solutions.

FIG. 7.



Generally speaking, two ways of effecting this object are practised; that is to say, the one solution can be poured into the other, or both run into the vessel at the same time.

In the first process the solution to be precipitated is already in the working tank, and is precipitated by the other solution, which may consist of one or several solutions together. This process is the simpler one, and therefore mostly used in practice.

In the second method the liquids are allowed to run into the precipitating tanks by taking out the plugs or opening the valves of the dissolving vessels simultaneously. It is essential that the outlet openings correspond with the quantities of the solutions in both cases. Otherwise it might easily happen that one of the liquids would be temporarily in excess, which in many cases must be strictly avoided. From the foregoing it follows that the process not only entails the use of more complicated appliances than the first one, but also more care and labour. Its application is therefore confined to cases where it is distinctly necessary for the preparation of special products.

If the solution tanks are provided with suitable small outlets, the foregoing method is sometimes preferable to the first one, as far as the inflow of a thin regular stream has a favourable influence on the fineness of grain, and consequently on the smooth fracture that customers very often require. The liquids cannot be so uniformly poured by hand, and therefore the formation of the precipitate proceeds irregularly, one part being fine-grained and another in bulky masses, so that the finished dry colours show an uneven, radial, or jagged fracture. Besides, it is only in the case of a few colours that smoothness of fracture is a reliable indication of fineness of grain, this applying especially to the pale chromes and the various kinds of Paris blue. Generally, however, the smooth fracture of the lumps depends too much on the structure of the colour in question for the fracture to be a reliable guide to the fineness, for most colours can be made with exactly the same fineness and covering power as the pale chromes and Paris blue, though the lumps will never exhibit a smooth fracture, owing to the fact that the structure of these colours is too loose for them to form compact lumps.

The disadvantages of the former method of uniting the solutions can be removed in two ways: either by producing the solutions themselves in a very dilute condition, or by thoroughly stirring the solutions, so as to ensure the rapid distribution of the precipitated bodies.

A continuous and thorough stirring of the liquids during the precipitating processes is, with few exceptions, a condition *sine quâ non* for a good result, and one need not be afraid of overdoing it. In the first place, stirring facilitates the mixing of the liquids, and therefore, as already shown, produces a finer division of the precipitate, which contributes equally to the brilliancy of the colours. This favourable influence of a thorough stirring, which is so important in the production of even simple colours, is still more so in the case of compound colours, in which there has also to be considered the question of efficient mixing with the other substances, which mostly serve as carriers of the colour (bases). A great number of colours are, in fact, prepared by precipitating the colouring matter from the solutions direct on to carriers, like barytes, white lead, red lead, &c.; and as these substances, owing to their high specific weight, are inclined to settle down very firmly at the bottom of the working tank, a continued stirring of the liquid in which they are contained is necessary to prevent this deposition.

The manufacture of compound colours, which can be considered as more or less diluted pure colours, such as lower qualities of chromes, Bremen blue, Paris blue, chrome green, &c., is based more especially upon the experience that a more intimate mixture of the pure colour with the carrier can be obtained with greater ease by the wet process than is possible by dry mixing. For this purpose the bodies serving as adjuncts or carriers are mixed with water, and put in the working tanks, where they are kept suspended by continual stirring, the colouring substances being then directly precipitated upon them from solution. The carrier (or "base") in this operation has to be brought into direct contact with at least one saline solution, and, being then regarded as in a state of solution, is treated accordingly. If this solution be now precipitated by another solution, the resulting coloured precipitate will envelop every single particle of the base in such a way that the original colour of the latter disappears.

The resulting new colour, which must be considered as a mixture, appears lighter or darker than it is in the pure state, according to the original lighter or darker shade of the base. The envelope covering the separate particles of the substratum will be the more perfect in proportion to the fineness of division of the resulting colouring precipitate and to the dissemination of the base. To obtain these results in the highest degree it is essential to work with very dilute solutions and to keep the whole liquid in continual motion in the working tank. In other words, the liquid must be continually and thoroughly well stirred during the process of precipitation, as well as after precipitation is completed.

The prime conditions, therefore, for obtaining a perfect product are great dilution of the saline solutions used for precipitation, and continual efficient stirring during and after the formation of the colour. In all cases where the result has failed the failure must be ascribed to neglect of one or other of these conditions.

This rule applies, with few exceptions, to all colours produced by the precipitation process, no matter whether they are prepared in a pure state or as mixtures with other bodies. In practice it is sometimes very difficult to keep such large dissolving tanks for every single salt, or at least for salts belonging (chemically) to the same group, as the extreme dilution of the solutions necessitates. This, however, can sometimes be remedied by filling the precipitating tank (which then, of course, must be very large) half full of water, and afterwards introducing the solution of salt for precipitation through a fine sieve.

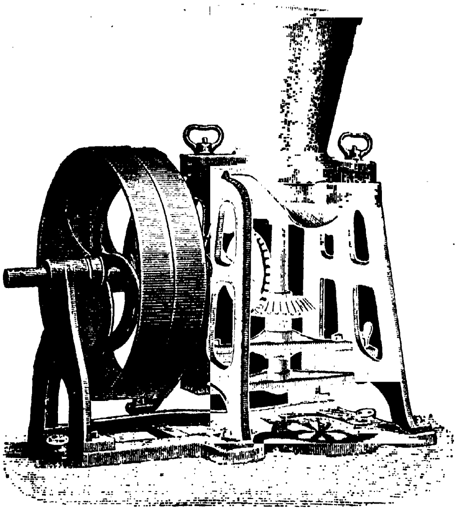
The advantage of this method is that at least one of the solutions can be diluted to a far greater degree than is possible in the ordinary way of manufacturing in special dissolving tanks. At the same time the second solution can be kept more concentrated without any ill effect on the resulting colour. Experience shows that it is quite immaterial whether a colour has been prepared from solutions that have been diluted as much as possible or whether one of them has been twice, three, or more times as strong as the other. *The sole decisive factor for a satisfactory result is the total quantity of water used in making the colour.*

The accuracy of this view is best illustrated by an example.

Suppose that a certain brand of chrome is to be produced in accordance with a formula specifying 2000 parts by volume of water. It will be immaterial to the shade of the resulting yellow whether the sugar of lead and the corresponding quantity of bichromate of potash are each dissolved in 1000 parts of water or whether the tank is filled with 1000 parts of water and the sugar of lead and the bichromate of potash are each dissolved in 500 parts of water, since in either case the total quantity of water prescribed for the operation amounts to the same—namely, 2000 parts. Where the working space is limited the proportion can be altered to still greater advantage by running, for instance, 1500 parts of water into the working tank, and dissolving each of the salts in 250 parts of water. Apportioning in this way the amount of water allotted for dissolving the raw materials, we obtain a means for reducing the dimensions of the solution vessels to a minimum—a circumstance of great importance to colour-makers working with only a slender capital or hampered by want of space.

As already remarked, it is specially important in the manufacture of mixed colours to have the added raw materials, such as barytes, gypsum, chalk, kaolin, clay, &c., introduced in a finely divided state. This condition can be most simply realised by first making the weighed quantity of additional matter into a paste in a suitable wooden vessel, preferably a cut-down petroleum barrel. This paste must be diluted with water until it assumes such a thin liquid consistence that it can be passed into the working tank through a fine sieve. When the final remainder of the liquid is in the tank the prescribed quantity of water must be made up if this has not been already done. In this way the additional matter is distributed sufficiently to allow in most cases the colouring matter to be absorbed without any difficulty.

FIG. 8.



The foregoing especially applies to minerals which can be easily ground in the dry state, the fine powder considerably facilitating the aforesaid process of preparing the base. Owing to their crystalline nature, these materials—for instance, barytes, chalk, &c.—are not difficult to form into a paste with water, whereas the case is different with most of the argillaceous raw materials, the very rich clays in particular. As they can very seldom be ground in the dry state, these must therefore be generally used in the form of irregular lumps and fragments. The difficulty of working these materials in the above-mentioned manner would be still greater were it not that all these clays, when left a long time in contact with water, change spontaneously into a soft, pasty condition. Even, however, in this state clays, and especially the rich kinds, are always difficult to work. The paste made by softening is generally so slimy and adhesive that much time and water are consumed in passing the clay paste through a sieve of the requisite fineness for colour-making. This difficult work, however, can be considerably simplified by grinding the clay paste again in a big hopper mill (Fig. 8) or (in larger works) a so-called wet mill (Fig. 9).

The former, which may also serve to grind dry colours with varnish, is known to all painters, and is in such general use that every important colour firm possesses several of these mills, so there is really no need to give a detailed description.

The wet mill is identical in principle with the mills used for grinding corn, tan, logwood, dry colour, &c. In this system, too, the stone runner, *A*, rests freely, by means of a fast or loosely embedded plate, *H*, on a vertically adjustable shaft, *E*, which can be regulated by the setting bar, *R*, and the adjusting screw, *S*.

The lower mill-stone, *B*, is recessed all round its periphery to a sufficient depth to make a water-tight joint with the vat-like wooden casing, *C*, which is bound together by iron hoops. The grinding stone is driven by the vertical shaft, *E*, actuated by cog-wheel gearing fitted with a stop motion. In using the wet mill the tank, *C*, is filled about half full with water, which, when the stone begins to move, gradually advances in the same direction as the latter. The materials, suspended in water, are then run into the mill. A baffle, *D* (Fig. 9), a shaped, thick piece of board, of hard wood, and perforated with holes, interrupts the circular motion of the liquid, and guides it into the breast of the grindstone, thus feeding the solid material to the stones to be ground. This operation being repeated continually, a short time frequently suffices to transform, by aid of the wet mill, even the most sticky materials into a finely divided, uniform, and more or less fluid mass. When the operation is finished the mass is run out through a vent or tap into a vessel underneath.

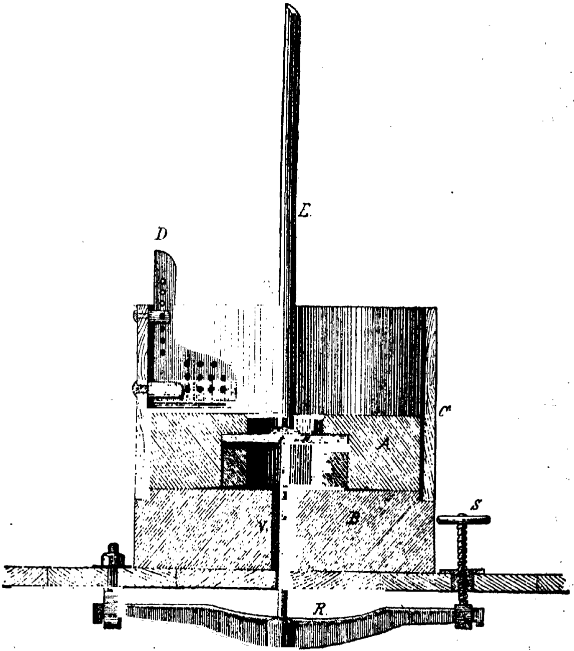
The Washing Process.—After the colours are made they have to be washed more or less repeatedly to remove the soluble by-products formed in the process of precipitation. Pure water is preferably used, other liquids being rarely employed. The water may be cold or hot, according to the mode of manufacture or the sensitiveness of the colours to high temperatures. In both cases the duration of the process and the result obtained are usually identical, the maintenance of a certain fixed temperature having, as a rule, no influence on the successful performance of the washing. If, nevertheless, a fixed temperature be prescribed for certain colours, this is due to the fact that the technical quality of the colours in question would be disadvantageously affected in some way or other by other temperatures than those mentioned.

The duration of the washing process depends, first of all, on the physical character of the precipitate, and more especially on its higher or lower specific gravity, its more or less distinctly crystalline nature, and on whether the by-products formed during precipitation are present in such quantity and concentration as to prevent the proper settling of the colour.

Whilst dense or crystalline colours can usually be thoroughly washed in a few hours, others that are more finely divided, and often specifically lighter, will require many days, or even weeks, before they have been washed free from all the adherent salts tenaciously retained by the mass.

The washing process can be performed either in the working tank or in a filter. The method selected depends entirely on the structure of the colours, although, generally speaking, neither has any special superiority over the other. As a rule, the precipitates which from their nature are difficult to wash present exactly the same difficulties in the filter as they do in the tank. It may be assumed that, with few exceptions, colours that settle down quickly to the bottom of the tank will filter quickly, and allow the washing water, added gradually on the filter, to flow away rapidly.

FIG. 9.



A, runner.
B, lower stone.
C, wood casing.
D, baffle.
E, driving shaft.
S, adjusting screw.
R, setting bar.
V, spindle packing.

The settling of the precipitated colour ensues the more rapidly in proportion as the washing process advances, because in proportion as more of the soluble saline matter has been removed the lighter will be the specific gravity of the more dilute solution formed by the freshly added washing water. The diminution in the saline content of the washings progresses very rapidly. Let us assume that in a tank filled to a depth of 64 ins. the mother liquor contains 22 lbs. of dissolved salt, and has been drawn off down to 16 ins. Leaving out of consideration the space occupied by the precipitate of colour, the remainder of the mother liquor still contains about a fourth of the original saline content—*i.e.*, 5½ lbs. This remainder is diluted threefold by filling the tank up again with pure water to the height of 64 ins. If now the washing water be again drawn off down to a height of 16 ins., there remains one-fourth of 5½ lbs.—namely, 1·4 lbs. of dissolved salt. The second washing water will therefore contain this quantity of salt dissolved in the entire contents of the tank, and when drawn off in turn down to a height of 16 ins. there will only remain less than half a pound of the salt—a quantity of no practical importance in most cases. From a practical standpoint preference should, for many reasons, be given to washing the finished precipitate direct in the working tank rather than in the filter, more particularly with regard to the desirable economy of space. In order to obtain a satisfactory result by washing in the filter, the thin paste of colours should be divided among a greater number of filter bags, and this cannot always be done without rather large rooms. On the other hand, much waste may be caused by this subdivision of the precipitate, the more so because the restriction of space in the workrooms hinders the movements of the workmen. Much waste is also caused through material remaining in the filter when emptied. Moreover, the process of washing in filters shows up in a worse light when considered from the theoretical aspect of the washing process. In a theoretical sense this process goes on in such a manner that the saline by-products contained in the precipitated colour are absorbed by the repeated additions of water, so that the solution becomes more and more dilute, and the saline matters are gradually removed by the repeated withdrawal of the washings. Consequently the washing process will be finished when the quantity of salts passing into the washing water has become so insignificant that their presence can no longer be revealed by the analytical means at present at our disposal. Of course, these salts are not only present in the supernatant water, but also in the precipitate itself, which is assumed to retain larger or smaller quantities of the dissolved salts, according to its physical structure. As a matter of fact, experience shows that the quantities of salt retained by the separate particles of the precipitate vary inversely with the crystalline character of the precipitate itself, and it may be assumed that the precipitate will correspondingly retain the enclosed salts more tenaciously during the washing process. On the other hand, the removal of these quantities of salt will be the more easily effected in proportion to the intimacy and frequency of the contact between the individual and finest particles of the precipitate and the freshly added water. This can only be accomplished thoroughly by washing in the working tank itself, since here the thorough stirring of the whole mixture brings both liquid and precipitate into continued contact with fresh quantities of the washing water, and the operation can be repeated *ad infinitum*. Such effectual stirring cannot, of course, take place in the filter, and therefore this method is placed at a decided disadvantage.

It might, however, be pointed out that in the latter method the added quantities of fresh water, in passing through the filter, are compelled to traverse the whole mass of the pulpy colour, and should therefore come in contact with every particle of the precipitate too. This opinion, however, is correct only in such cases where the nature of the precipitate allows the washing water to percolate through without any special difficulty. In such event, as already mentioned, this method of washing is by no means inferior to that in the precipitating tank. However, it easily happens with finely divided clayey or slimy precipitates, such as Paris blue, &c., that the meshes of the bolting cloth become clogged with the precipitate, and in consequence the action of the washing water is diminished. Even this is not always an essential preliminary, the collection of a thick coating on the filter being often sufficient to prevent the passage of the washing water, so that a proper washing is out of the question. This may occasionally be remedied by removing the mass from the bolting cloth, but usually the improvement is only of brief duration, the trouble in question soon reappearing. It is therefore evident that slow filtering colours need special attention in washing on the filter, and as this is not always feasible, especially in small works where there is no night shift, a considerable loss of time is involved.

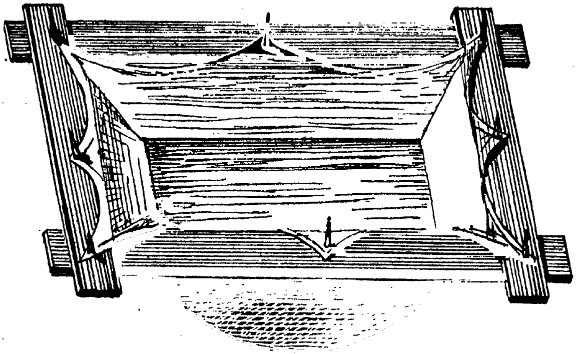
None of these misfortunes need be feared when the washing is performed in the tanks direct, and although the washed colour only settles down very slowly the separation of the adherent salts will at any rate be more complete. The consequences of omitted or insufficient washing mostly appear only after the colours have been dried, these latter becoming extremely hard. The residual salt cakes the particles of colour together, or when these are moulded into regular blocks dark-coloured, white, or metallic shining spots and stripes are formed, which can no longer be completely removed, except, perhaps, by scraping off, with a considerable loss of time, later on. With pulp colours, too, the consequences of faulty washing can be observed, especially when they are exposed to the air for some time; they then get covered with a coating of fine crystals, which sometimes decompose through exposure to the air.

Sometimes the effluent water still contains a sufficient quantity of dissolved salts to make their recovery or remanufacture profitable. To allow such lyes to run to waste would therefore be uneconomical. The recovery can be effected by evaporating these solutions and separating the salts by crystallisation, or precipitating the base of the salt in a form suitable for direct application. For instance, a lye still containing large quantities of barium chloride may be precipitated with sulphuric acid for the recovery of *blanc fixe*. By taking this into consideration in establishing a new works, one of the drying rooms can be fitted with a large flat evaporating pan, heated by steam pipes, taking up comparatively little space. The cost of attendance will be small, the work being supplementary to other tasks, and the prime cost will soon be liquidated.

Filtering and Pressing.—After it has been ascertained that all the salts adhering to the precipitates have been eliminated by washing as described above, the next step is to free the colours, as much as possible, from the final traces of contained water. This can be done to a certain extent by the operation of filtering—namely, by passing the liquid containing the pulpy colour through some porous material which allows the liquid, but not the solid matter, to pass through its pores. These porous materials are called filters, the effluent liquid is the filtrate, and the compact mass remaining on the filter is the residue.

In laboratory practice white, unsized, and therefore very porous paper is used for this purpose, and is known as "filtering paper." For technical use, however, a firmer and stronger material must be used, preferably consisting of a special closely woven three-shaft linen, cotton, or woollen fabric. The desired fineness or closeness of these fabrics varies with the nature of the materials to be filtered, and therefore the same woven material cannot be used for all colours. In filtering colours of very fine grain it frequently happens that at first the colour passes through pores of even the closest fabric, the filtrate not beginning to run off perfectly clear until the pores of the filter cloth have become so far obstructed as to preclude any further percolation of the colour. On the other hand, ordinary linen cloth can be safely used for filtering certain colours, such as zinc yellow, Bremen blue, &c., and therefore economic reasons will dictate for such colours the use of cheaper fabrics than are required for colours of very fine grain (for instance, Paris blue, pale chrome, &c.).

FIG. 10.



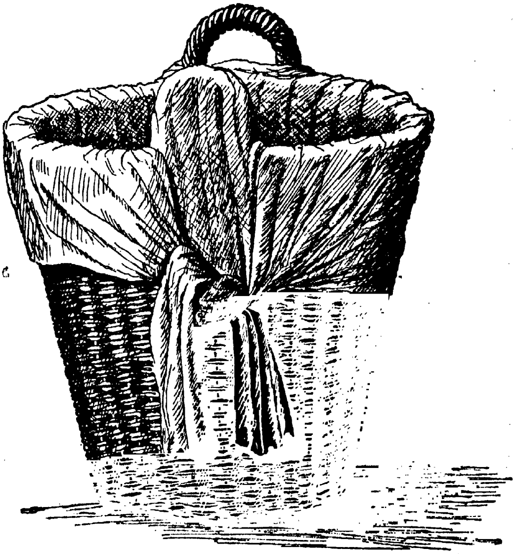
The fabric is used in the form of square cloths, as well as in the shape of pointed bags, according to the quantity of the substances to be filtered. The decisive factor in the choice of shape is in all cases the ease with which the filter residue, which alone has to be considered, can be recovered. For this reason preference must always be given to the square filtering cloth as compared with filter bags, because in the first place the pressing process, which will be described later on, can be effected more quickly and conveniently by means of the former.

In both cases the filter is fastened on to a framework of smoothly planed laths or rods of suitable hard wood. At the joints the rods are connected by means of long nails, the points of which latter should project through the wood far enough to afford a hold for the filtering cloth or pointed filter bags on the four edges (Fig. 10) when the frame is inverted.

Filters of this kind will only succeed with small quantities. At a big colour works they are quite insufficient. Here, to filter large quantities of colours, suitable filtering cloths of a square shape (60 to 80 ins. square) are employed, and these are spread over large circular baskets so as to cover the sides of the latter all round symmetrically and turn over the outer edge about 4 ins. all round. The ends of the cloth must be tied together, two on each side, directly below the handles (Fig. 11). By this easy method a filter is obtained which, in spite of its simplicity, does its work thoroughly. The first striking advantage of this arrangement is that the baskets can be placed anywhere without difficulty. Another is that the colour paste remaining on the filter can be taken away, together with the cloth, and put directly into the press.

On filtering certain substrata—alumina, for instance—which are constantly required in large quantities and in the form of paste (about half water), it is advisable to use large flat wooden chests, with fluted sides and perforated bottom. A large filter cloth is spread, and the precipitate to be filtered is introduced. Such an arrangement gives the advantage of having the filtering apparatus combined directly with the storage tank, thus saving much time and material.

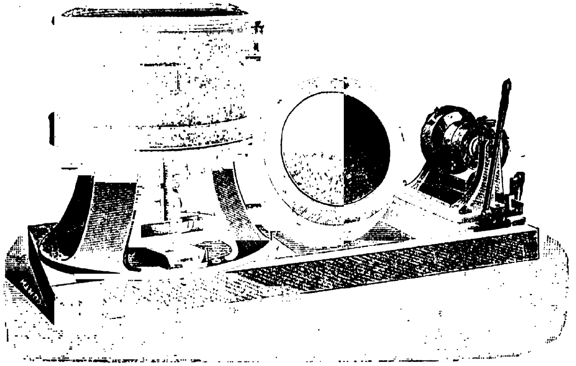
FIG. 11.



The different faults inherent in all filtering devices, to which we have already referred in connection with the different methods of washing, have naturally led to improvements for more or less completely overcoming those defects. First, an attempt has been made to accelerate the filtering process, which is very slow in the case of many colours, by means of compressed air, aspirators, &c. Only two, however, of the many more or less complicated forms of apparatus constructed for this purpose have found general application in the colour industry, and even these are not faultless. These two are the filter press and the centrifugal machine, or hydro-extractor.

The latter can only be used for homogeneous colours, but these it both filters and washes perfectly. Diluted colours, however, settle down on the filter of the centrifugal machine in different strata according to the varying specific gravities of the component bodies—the heaviest first, then the medium weights, and finally the lightest. For instance, when any kind of chrome green (made from barytes, chromes, and Paris blue) is treated on the centrifugal machine, there will remain on the filter stripe, after the expulsion of the filtrate, a paste in three distinct layers, composed, first, of the barytes, as the specifically heaviest body; next, the lighter chromes; thirdly, the Paris blue, which, owing to its fine grain, retards the process of filtration, and therefore settles down last. Figs. 12 and 13 represent a centrifugal machine.

Fig. 12.

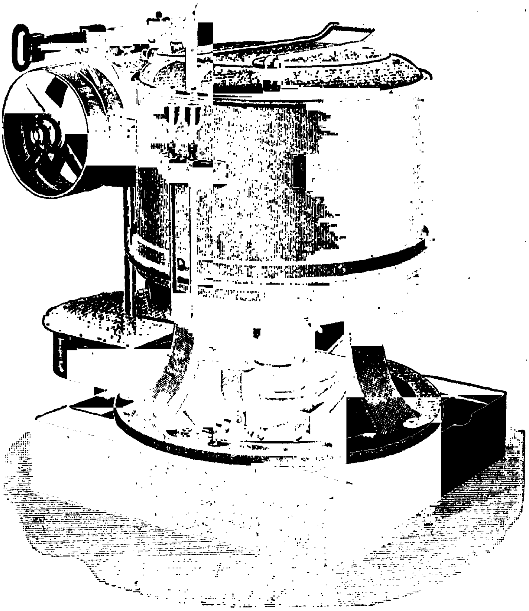


Though the filter press does not possess this fault, and has undeniable points of superiority, it cannot be used for filtering and pressing every kind of colour. In particular a great number of chromes suffer considerable change with regard to quality and shade after having been treated on this machine, inasmuch as they darken considerably, but unequally throughout the whole mass. For this reason these chrome greens assume an olive-green shade in the filter press, and similar drawbacks occur with many other colours.

For colours, however, of a less delicate nature, such as Paris blue, *blanc fixe*, chrome orange, and most of the aniline lakes, &c., the filter press offers great advantages, since it performs three operations at the same time—filtering, pressing, and washing. Through the employment of pressure all such colours as are generally very difficult to filter can be treated with ease, and in a relatively short time, with perfectly constructed filtering presses.

Centrifugal machines for colour-manufacturing are made in two distinct patterns, the driven type (Fig. 12) having been found the best in practical use. The drum, perforated like a sieve on the side walls, is covered with a close filtering cloth right up to the top of the casting, especially when the machine is used for large quantities of material; then the pulpy, more or less fluid colour is fed into the machine, and the contained water is thoroughly expelled by setting the machine to run at very high speed (1200–1500 revolutions per minute). When the drained colour is to be washed in the machine the drum must be refilled with pure fresh water and kept in rotation until the final traces of washing water have been forced through the colour and the filter cloth. This operation can be repeated as desired.

FIG. 13.



Where room is scarce the type of centrifugal machine illustrated in Fig. 13 is suitable. This machine is designed specially for such a contingency, and takes up very little room.

The first firm to build centrifugal machines as a speciality was C. G. Haubold, Jun., Chemnitz, whose machines have a high reputation.

The principle of the *filter press* is to present large filtering surfaces to extremely thin layers of the mixture of finely divided solid bodies and liquids. This problem is solved completely by a systematic arrangement of narrow detachable chambers connected together by channels. The broad sides of these chambers are lined with filter cloth, which separates the mixture of pulpy colour and water (introduced through the channels under a high pressure) by retaining the colour paste in the chambers whilst allowing the water to escape through the pores of the filter cloth and drain away through lateral channels. The percentage of water in the paste depends on the amount of pressure applied, and can be varied according to requirements.

In practice two chief systems of filter presses are used, viz., *frame presses* and *chamber presses*. In the former a number of small frames are held in position between solid plates, wherein the press cakes will be formed, the latter being afterwards taken out along with the frame. In the chamber presses, however, the narrow chambers in which the colour paste collects are formed by arranging a number of symmetrical plates, in the form of shallow boxes, in pairs. On opening the press after the operation is finished the cakes of colour fall into a wooden box placed underneath.

FIG. 14.

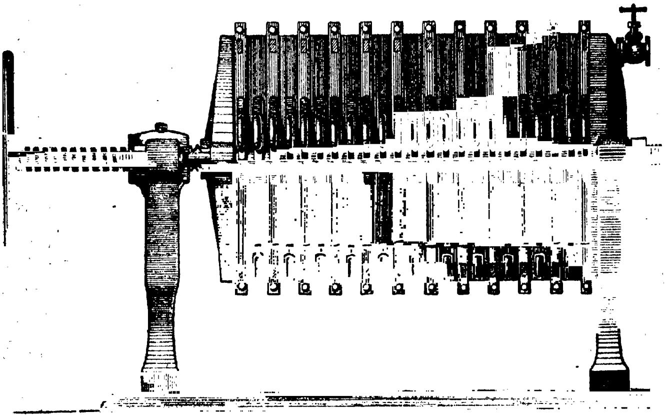
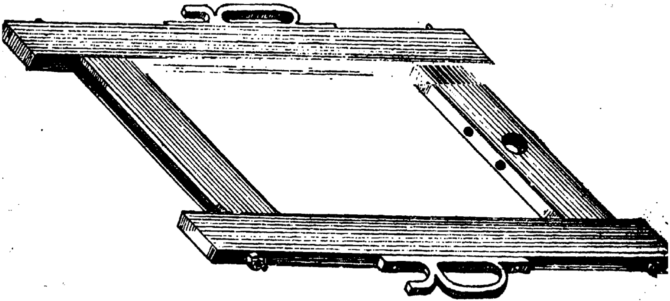


Fig. 14 shows a frame press in the closed state, while Fig. 15 represents one of the frames and Fig. 16 the corresponding filter board. Fig. 17 is a cross-section showing the internal arrangement of the frame filter press when closed. To set the filter press to work, the filter frames, *R*, are inserted alternately with the filter plates, *B*, a strong filter cloth, *T*, being suspended in the frame of the press and forced against a strongly fixed head-piece by the aid of a strong screw spindle or worm, whilst the joints between the filter frames and plates are packed sufficiently by the filter cloth, *T*. By means of a pump provided on the head of the frame, the liquid to be filtered is introduced into the channel, *C*, *C*, formed by the several parts of the press, and passes through openings provided in the frame (Fig. 15) into the intermediate space formed by the filter frame, *R*, and the filter plate, *B*. Here the separation of the solid body from the liquid takes place. The latter penetrates through the pores of the filter cloth, then along the ribs of the filter plate, *B*, and into the openings of the conduit, *H*, from whence it reaches the outside through the brass or wooden valve provided on the conduit. The solid colour, however, remains between the several filter cloths, and consequently forms a solid cake, which is firmer in proportion as the working pressure is increased. When the press is full, the closing screw is released, and the colour cakes may be taken out along

FIG. 15.



with the frame, and, after being cut out, can be removed for drying. The press is then put together again in the same manner and recharged with fresh liquid.

The frames and filter plates for this purpose are preferably made of strong wood, the frame being held together by iron rods (Fig. 15). To prevent the wood warping or cracking it is advisable to keep the filter press always shut when not in use. The filter cloths should, of course, always be washed before being used.

In large works vacuum filters are sometimes used.

These filters consist of large square chests with double bottoms. The upper bottom, of wood or metal, is perforated, thus forming a kind of sieve. This is covered with the filter cloth, spread so as to lap over the edges of the chest. Between the upper and lower bottom is left an empty space of medium dimensions, which can be hermetically shut from the outside air, and is connected with a suction air-pump. The colour paste is laid on the filter cloth, and the surplus water is allowed to drain away. As soon as the water ceases to run the air-pump is set going, and exhausts the air from the space between the two bottoms. The suction also extends to the colour-paste, and draws out all the contained water; and finally, when all the water has been removed, the air drawn in through the colour by the air-pump exerts a drying effect. Apparatus of this kind is used in colour manufactories to only a limited extent, despite its undeniable advantages for many kinds of colour.

An innovation in filter apparatus is afforded by the *filter stones* introduced by William Schuler, of Isny (Württemberg). These are porous stones which retain all solid matters, whilst allowing all liquids to drain through. The stones are compound in structure, and capable of resisting the action of strong and even concentrated and hot acids, and also alkalies of moderate strength. The principle of filtering through stones has been applied for purifying water, but the Schuler filtering stones are made in a different way from those, inasmuch as the whole mass is not of uniform porosity throughout, the surface being close in texture, varying according to the material to be filtered, whilst the lower strata are coarser. In this way the perfect retention of the filtered residue is ensured, together with an unrestricted outflow of the filtrate. These stones are suitable for filter chests as well as for the porous bottom of the vacuum filter. In this form they have been much used in colour manufactories, and their greater durability renders them more economical than filter cloths.

FIG. 16.

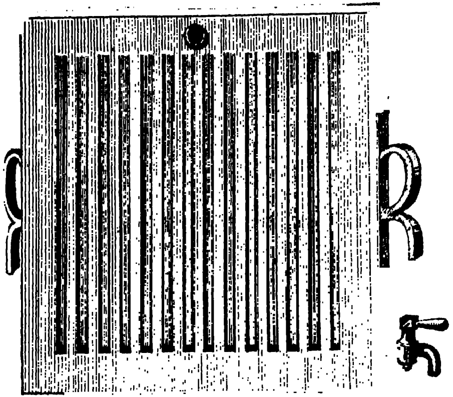
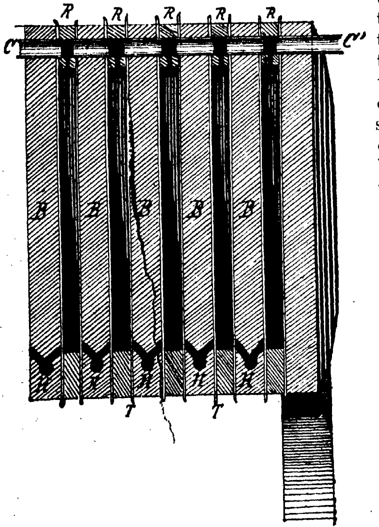
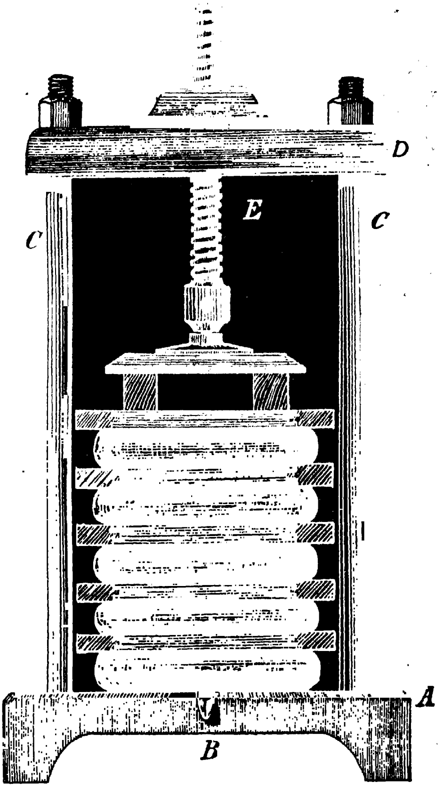


FIG. 17.



The suitable pressing of the colour paste taken from the filter is by no means such an easy matter as one might think, and cannot be left to any ordinary workman without careful expert supervision. Apart from the fact that a well-pressed colour paste can be worked—*i.e.*, comminuted—much easier and quicker, for the purpose of removal into the drying-room, than imperfectly pressed paste, a thorough removal of the moisture below the press is essential, since it naturally accelerates drying. Any unnecessary delay in the drying process is very injurious to most colours. The reduction of the moisture content of the colour paste before it reaches the drying-room is therefore of great importance, and should be carried out as effectually as possible. There is only one way of doing this, namely, by properly treating the pulpy colours in a press, and this operation must therefore receive as careful attention as any other in the preparation of colours.

FIG. 18.

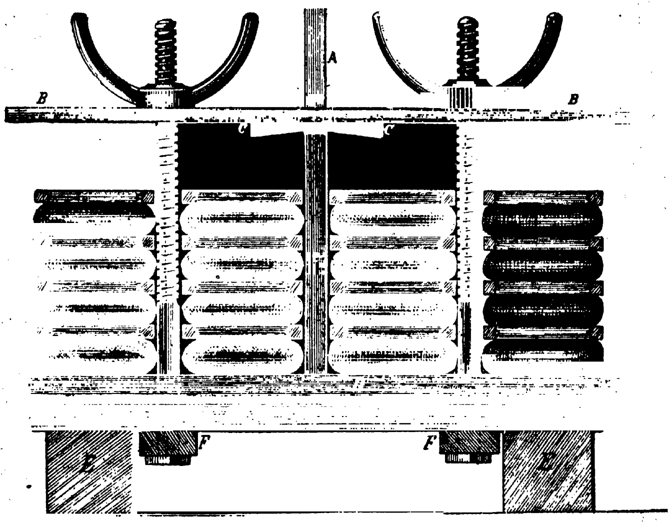


Another point is that all colours cannot be pressed in the same manner or in the same time, many of them opposing considerable difficulties to this operation. To this class belong all those substances which (as in the filtering process) exhibit the troublesome peculiarity of obstinately retaining mechanically admixed moisture. It may be assumed, therefore, that such colours as are in general difficult to filter will behave similarly in the press, this latter treatment being really nothing else than an accelerated process of filtering; consequently the same rules may be applied in both.

The selection of apparatus for pressing the colour paste is not a matter of indifference, although any type of press would give results of some kind. In this case, also, simplicity, ease in working, and economy of time are the decisive factors. As already mentioned, the filter press can only be used for a limited quantity of colours; and, again, in spite of its indisputable efficiency, the very high price of this machine is a drawback for small works, at least when starting business. For the former reason, moreover, large colour works are forced to keep, in addition to the filter press, certain other appliances capable of doing the same work, even though in a less perfect manner. Of the innumerable machines of this kind (especially hand-presses), there are two which have proved highly suitable ever since the beginning of the colour-manufacturing industry, owing to the very simple manner in which they are worked ; and these will now be described.

Fig. 18 represents a hand-press of the simplest possible type. The chief parts are made entirely of iron, and, owing to the small space occupied, and the relatively small weight, this press can be used in any disposable place. The whole apparatus consists of four parts, viz., the square plate, *A*, provided with four feet, a channel running all round, and a spout on one side ; the heavy round iron pillars, *C*, *C*, carrying the female screw or nut, *D*; the powerful screw spindle, *E*; and the aforesaid female screw, *D*, which is also made very strong. The head on the lower end of the screw spindle is bored through in two directions, is provided with a terminal stud, and is made much broader than the screw spindle itself.

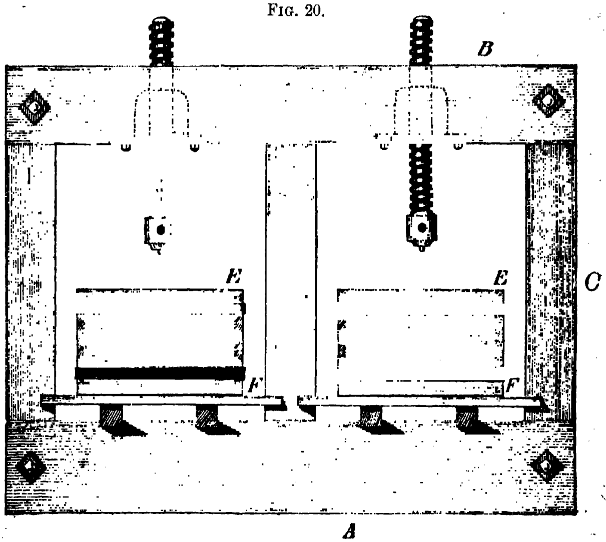
FIG. 19.



The holes in the head serve the purpose of tightening the screw spindle by means of a fairly long round iron bar, which is inserted in the holes and enables any desired amount of pressure to be imparted to the spindle. In order to transmit this pressure to the colour paste in the press, the stud at the end of the spindle fits into a recess in an opposite plate, which is screwed on to a suitably strong oaken board, which can be removed at any time.

The colour paste is put into filter cloths or filter bags, and the "cheeses" thus formed are piled up one above another, a board being inserted between each pair. When the press has been filled with about five or six of these press-cakes, two strong blocks of wood are put lengthwise over the top board, and the recessed plate is laid crosswise over all, as shown in the sketch. The screw spindle can now be tightened, slowly and carefully at first, then with gradually increasing pressure, until finally no more liquid drains off. Throughout the whole extremely simple operation the only care needed is to see that the press-cakes are placed exactly one over another, so as to distribute the pressure from the screw spindle evenly on all sides. With a little practice this can be attained without difficulty. In spite of its simplicity, this screw-press answers its purpose extremely well, and moreover can be recommended for small works, because it will press even very thin layers of colour. This circumstance is of great importance, especially in view of the moulding of the pressed colour, an operation which will be described later on.

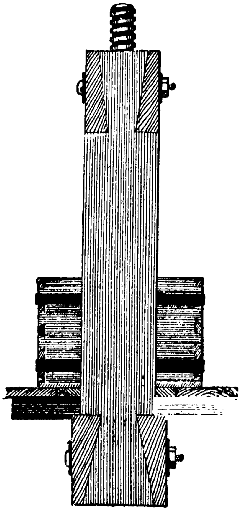
FIG. 20.



For larger works the same press can be made as represented in Fig. 19, and will then deal with considerable quantities of colour. The two screw spindles are fixed into the strong wooden frame, *EDE*, by the cross-beams *FF*. The necessary pressure upon the packs of colour paste is applied by tightening the two nuts which are provided with strong, bent handles for this purpose. The packs of colour paste are placed in the spaces left between the screw spindles and the upright beam *A*, which is fixed tightly into the base *D*. A loose board *B* is lowered by removing the wedges *CC*, and powerful pressure is applied by tightening the nuts, this pressure being evenly distributed to all parts of the press by the board *B*. At a certain height the beam *A* is provided with holes, to receive the wedges *CC*, which support the loose board *B*, that would otherwise be in the way while the press was being charged.

Another press of the same type (Fig. 20) is equally capable of dealing with large quantities. With the exception of the screw spindle and nut all the parts are made of oak, of a strength corresponding to the high pressure. As is shown in Fig. 20 the press consists chiefly of a frame made of strong beams. The method of joining the latter together is shown in Fig. 21, representing the front of the press, so that no further description is needed.

FIG. 21.



The bottom beam *A* of the frame is made stronger than the sides *B* and *C* for two different reasons. In the first place, it has to act as the foot of the press, and, secondly, to support the box in which the colour paste is pressed. The strong cast-iron nut is countersunk in and fastened to the top beam and centres the screw spindle in a perfectly upright position in the vacant space between the side beams. The press-box, *E*, is made of pine planks about 2–2½ inches thick, strengthened with strong iron hoops, and provided with an outlet for the effluent water just above the bottom; it rests upon a very strong board, *F*. The latter is about four inches broader all round than the bottom of the box itself. It should be provided with a fairly deep gutter all round, so as to collect and guide the effluent water in a definite direction.

The working of the press is very simple. The colour, having drained sufficiently, is taken out of the basket in the filtering-cloth and put into the press-box, so that each corner of the cloth fits exactly in a corner of the box. The cloth is then turned over inwards all the way round, the box being closed by a tight-fitting lid, the head plate is put on, and the screw spindle is tightened in the manner described above.

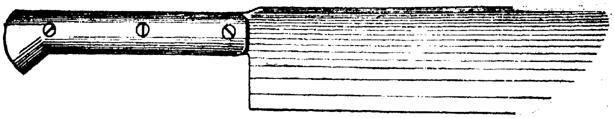
All the kinds of press used in colour works, the hydraulic press included, are based on the same principle, except that the power is applied in a different way. With regard to the use of hydraulic presses for colour works, attention may be drawn at this point to the fact that satisfactory results can, as a rule, only be obtained with small or medium size presses.

Moulding the Colours

It has always been the custom in the manufacture of colours to place the finished articles on the market in special and more or less attractive form, usually with the object of doing a larger trade in new varieties. How far such a course was successful in former times need not be discussed here;

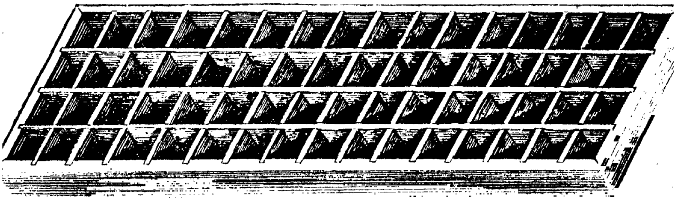
at any rate the users of colours at the present day cannot be induced, except in the rarest cases by the exterior form, to buy a colour from its appearance unless other proofs of its superiority are supplied. For this reason less importance is now attached by makers to the moulding of the colours than was the case a decade back, and it is only in the case of such colours (chiefly Lakes) as have become associated for years in the public mind with a certain special shape that are now usually sent out in that one particular form.

Fig. 22.



As a rule, the artificial mineral colours are made in only three forms, and that too only in the case of certain kinds. These are the better grades of chrome and white lead which are put on the market in the form of regular square, flat, or round cakes, or as large or small cones or drops. In addition to these chromes, the various kinds of Paris blue are frequently put on the market in the form of long narrow slabs, those of Bremen blue in the form of large rectangular lumps, chiefly because of the great difficulty in powdering this colour without serious loss of expensive material, and also in order to demonstrate the low specific gravity of the Bremen blue in a specially striking manner by the large size of the lumps. The satin greens too (a better quality of chrome green) are generally brought on the market in the shape of cones, in order to show up their superior quality in point of increased fineness and covering power in comparison with the ordinary chrome greens. This exhausts the series of specially shaped artificial mineral colours, and there are now only a number of Lakes as certain finer kinds of earthy colours, which are met with in other than the above-mentioned forms or in the shape of rods or corrugated lumps, stars, triangles, &c. To obviate the necessity for repetition later on in the book the process of moulding the last mentioned shapes will now be described. Square or rectangular lumps of colours can be made in different ways and without much loss of time. The pressed cakes coming from the filters or screw-press can be cut with suitable knives (Fig. 22) of wood or copper into symmetrical lumps, and dried

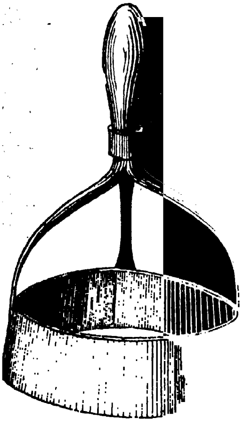
Fig. 23.



in this form. The colour paste, when not too stiff, can also be spread upon frames made specially for this purpose, divided into a large number of equal compartments (Fig. 23). The lumps are then dried.

The latter method of course gives very symmetrical pieces, but entails higher cost in making the frames, which is by no means unimportant. The colour in the compartments shrinks through the evaporation of the water, so that loose, half dried lumps are obtained, and these have to be turned over by placing the frames upside down on ordinary drying-boards, to facilitate drying. They are left in the drying room until the last trace of moisture has escaped. Then the perfectly dry lumps are scraped over with a knife on all sides, carefully, to brighten their appearance, and rubbed on coarse canvas which has been stretched tightly on the plate of the working table and fastened with nails.

FIG. 24.



Round lumps are obtained by cutting out with a tapered copper ring, fitted with a suitable handle (Fig. 24).

In this operation the press-cakes, especially if they have been produced in a screw-press, must first be suitably levelled and must not be thicker than the height of the cutting ring.

For making cones or drops the best apparatus to use are shown in Figs. 25 and 26. The first is a strong copper or brass plate hopper of medium size with a flat bottom, and fixed into a wood frame provided with a handle made out of one piece. This frame, of very strong wood, white beech for instance, carries, at the place where the handle commences, a peg about an inch long, made of the same wood, the purpose of which will be explained later on. The bottom of the hopper has a number of small circular holes, in which are soldered little pipes about half an inch long, about as thick as a pencil.

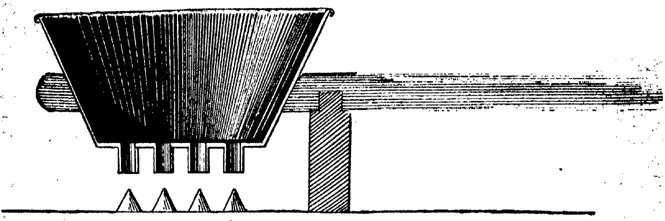
In working with this apparatus, first of all the colour paste must, to obtain the proper consistence, be rubbed through a fine brass sieve by aid of a wood spatula, and with this paste the hopper is filled. The shock produced by striking the said peg on a solid support presses the colour paste through the narrow pipes and it falls down, in the shape of drops, on to a piece of strong paper placed underneath. As soon as the paper is covered with the cones, the whole is transferred to a drying-board and taken to the drying-room. With a little experience the consistence of the colour paste necessary to furnish a good result will soon be ascertained.

The second apparatus, as shown in Figs. 26, 27, and 28, is usually constructed on the same principle. Instead of the hopper it has a large chest, the bottom of which is made of a strong brass plate, provided with a great number of tapered holes.

This chest is hung, by means of two solid arms, on a strong shaft *B*, which works loosely in the bearings *C* and *D*. The support of the bearing

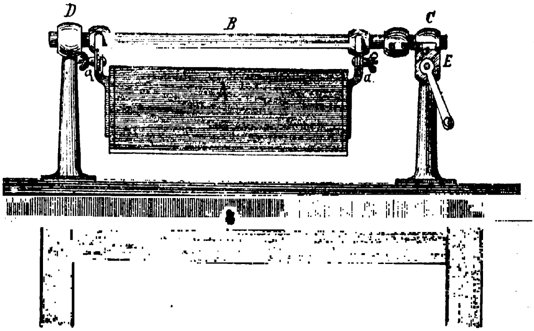
C is connected by a rod with the support *E*, which is placed a little lower down, and carries a crank. Between the support *C* and the nearest arm is placed a very strong second rod, tightly connected with the shaft *B*, and therefore obliged to follow the slightest movement of the shaft. Close

FIG. 25.



behind the support *E* the crank shaft carries a small shouldered cam *G*, on which the free end of the rod *H* rests loosely, as also the chest *A*, movable at *a* and a_2. On turning the crank *F* the cam raises the rod *H* and also the chest *A*, the latter falling back in its former position as soon as the rod (*H*) has passed the shoulder of the cam.

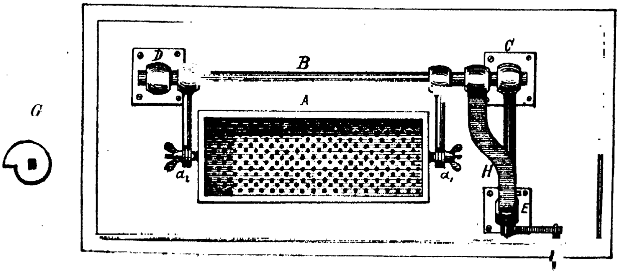
FIG. 26.



Since at this moment the free end of the rod *H* strikes a powerful blow upon the head of the support *E*, the chest *A* vibrates in the same manner as the hopper in Fig. 26 when the peg was struck. The same result is therefore produced, namely the colour paste is forced down through the holes in the bottom of the chest, and falls down in the shape of small cones to a piece of paper or a thin board underneath.

This apparatus gives a much larger output than the other. It must, however, be borne in mind in working it that the diameter of the cone and therefore the resulting blow must vary inversely with the specific gravity of the colour under treatment. A simpler construction of the coning apparatus is to hang the chest with the perforated bottom, not in the crank frame already described, but on cords or lengths of gut fastened at the four corners, and all of them running over a roller fixed on the ceiling or on a wall bracket. The chest, filled with colour paste, rests on strong feet about an inch high. It must be raised about 10 inches and let fall on to a paper on the working table. Where shafting is available the up and down motion of the chest can be effected by an eccentric or by cams like those used in stamp mills. This simplified coning-machine may be made of larger dimensions, so that a thousand or more cones can be made. Both the chest and the table underneath must of course be made particularly solid. The former should be of brass, the latter preferably of solid brickwork, covered with a metal plate.

FIG. 27.



Similar apparatus is used in making rods or corrugated lumps of Lake colours especially used for lithographic printing. Instead of a blow a proportional pressure should be applied on the prepared colour paste, which is thus forced through the circular or zigzag holes in the bottom, and thereby acquires the desired shape. Fig. 28 represents such an apparatus, the construction of which will be intelligible from the foregoing description. In small works, squirts, similar to cake syringes, are used.

All colours put on the market as irregular lumps or fragments, or in the form of a more or less fine powder, must, after being thoroughly well pressed, be cut by the aid of suitable knives or wood spatulas into small pieces, which are placed in this form on the drying boards and dried in a drying-room or, if the season allows, in the open air. Corrugated flat plates are mostly made in the filter press, the fluted walls of which press the ribs into the colour cakes.

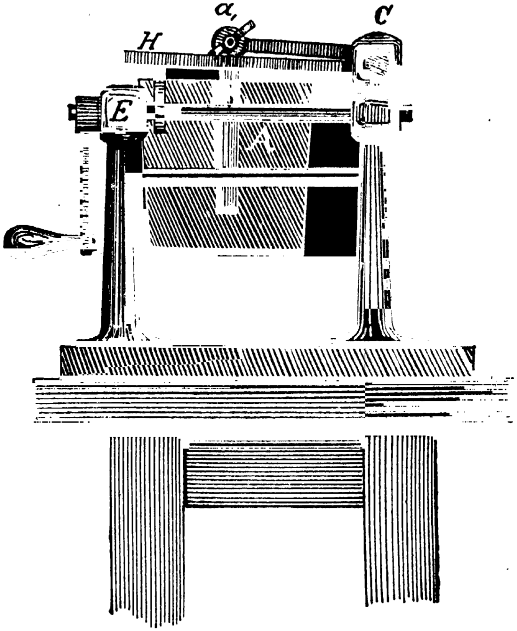
Drying the Colours

Of no less importance than the chemical composition of the artificial mineral colours is the method of drying employed, most colours, as already mentioned, being liable to a variety of changes even in the course of the drying process. These changes may go so far as to entirely spoil the dry colour.

Generally speaking, there are two chief methods of drying, viz., drying in the open air, and drying in closed rooms brought to the required temperature by artificial heat.

Of course, the first-mentioned process can only be applied in countries having a suitable climate, and where, as a rule, the summer is long and hot—for instance, in the South. In fact, this source of heat is very largely utilised in such climates. In all northern countries, however, the artificial heating of the drying-rooms must be resorted to, though sometimes the two methods can be combined—for instance, by manufacturing a large quantity of the most saleable colours in the summer-time, and drying them in the open air, the rest being dried in winter-time in heated drying-rooms. Colours that are sensitive to light cannot, of course, be dried in the sun.

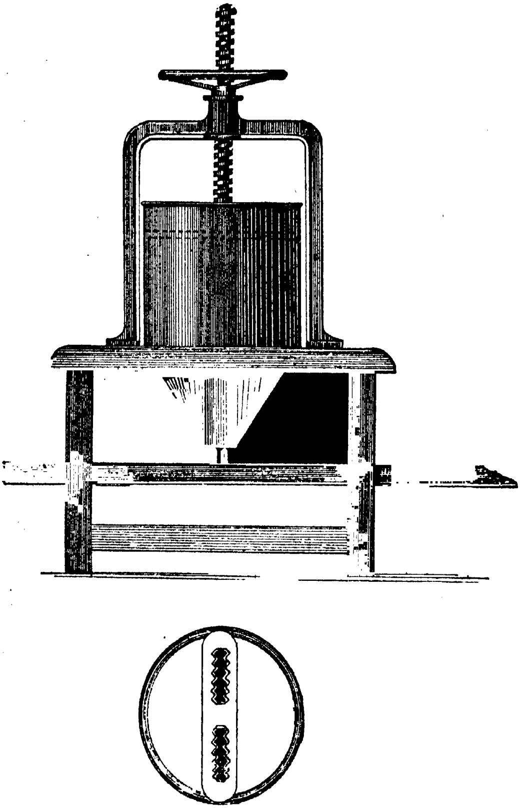
FIG. 28.



In both cases, whether natural or artificial heating be employed, the same form of drying-boards or frames is used, the drying-racks on which the boards are supported being also the same. The frames are simple boards about 40 inches long, planed on both sides and held together by two cross battens. They are provided on three sides with fillets about 1 inch high (Fig. 30). Open frames of the same length, and about 20 inches wide, covered with cloth (Fig. 31), are also used.

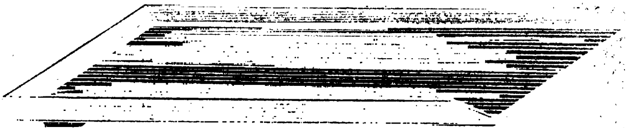
For many reasons the first style of frame behaves better in practice than cloth-covered frames. First, they can be more easily washed, and therefore

Fig. 29.



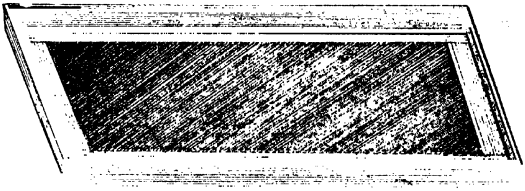
the same boards can be used for different colours of similar shades; secondly, they are more durable, and can be repaired, if necessary, much easier than the open frames. True, the porous material, by allowing unrestricted circulation of the air, facilitates a quick drying of the colours better than the solid boards. But this, as experience shows, is only correct for a very limited number of colours, and, as a rule, this advantage does not compensate for the disadvantages of the open frame. Drying-boards of perforated sheet-metal, or frames of wire-netting, are also suitable, and though they have to be a little smaller in dimensions, are handier, and have proved very satisfactory. To prevent rusting, the plates, frames, and fabric are tinned all over. Upon these the colour-frames are laid on strong absorbent paper, which can be kept for use over again for colours of the same shade. The netting and perforated plates admit warmth and circulating air, and the absorbent paper, besides drying quickly, also takes up a certain amount of water from the drying material.

FIG. 30.



The racks supporting the frames and drying-boards are made of wood throughout. They must be very strong, since they generally have to carry a very large number of drying-boards. The arrangement of these racks, for use in the open air as well as in drying-rooms, is shown in Fig. 32, so that it need not be further described. For use in the open air the rack must, of course, be provided with a suitably constructed protecting roof.

FIG. 31.



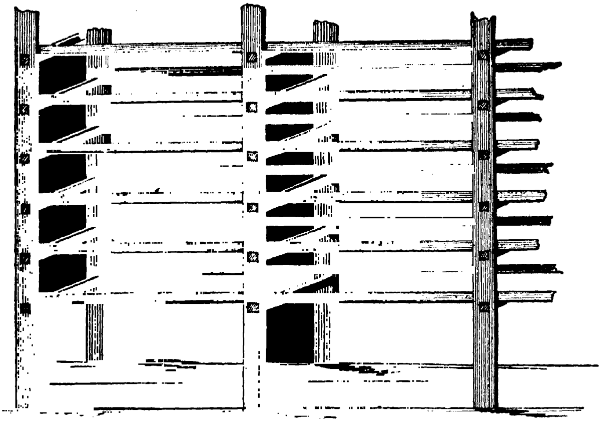
The heating of the drying-rooms or drying-stoves can be effected in two ways, either by direct fire (hot air) or by steam. In both cases it is an essential condition that the rooms should have strong and air-tight walls to prevent the escape of warm air. The most important point, however, to be considered in the arrangement of a "drying-stove" is efficient ventilation to enable sufficient quantity of fresh air to be supplied to the room at all times and to remove the moisture-laden air quickly.

The methods employed in practice vary so considerably that it is impossible to discuss each of them here, and we will therefore confine ourselves to two systems, both of which are distinguished by great simplicity and efficiency.

In choosing between these two systems of heating a large number of, for the most part, very important circumstances have to be considered. First of all, the peculiarities of the individual colours must be considered, since these do not always dry equally well with both systems—as can be observed in a marked degree with chromes and chrome-greens, for example. Whilst these can be dried by hot air without suffering any change in their properties, they will rarely do so satisfactorily under the same conditions in drying-rooms heated by steam. This fact can also be observed in the case of many other colours, but has never yet been satisfactorily explained.

The choice of the method of heating will also be influenced, of course, by the cost of fuel and the rate of wages. Heating by direct fire, of course, requires more attention than steam heating, since the latter can be regulated, without particular trouble, by any workman. Generally it may be said that direct fire heating, if properly looked after, is cheaper than by steam heating, the drying process being usually much quicker. This circumstance, in conjunction with the smaller risk of injury to the shade of the colours, should be sufficient to give this system of heating the preference. That this is not always done is mainly due to the risk of superheating and the danger of fire, which are entirely precluded in heating by steam. On the other hand, this latter system has the disadvantage that leaky pipes, valves, connections, &c., which can never be completely avoided, introduce moisture unnecessarily into the drying-room, which retards drying, the more so because the leaks are generally neglected until the escaping steam begins to be audible.

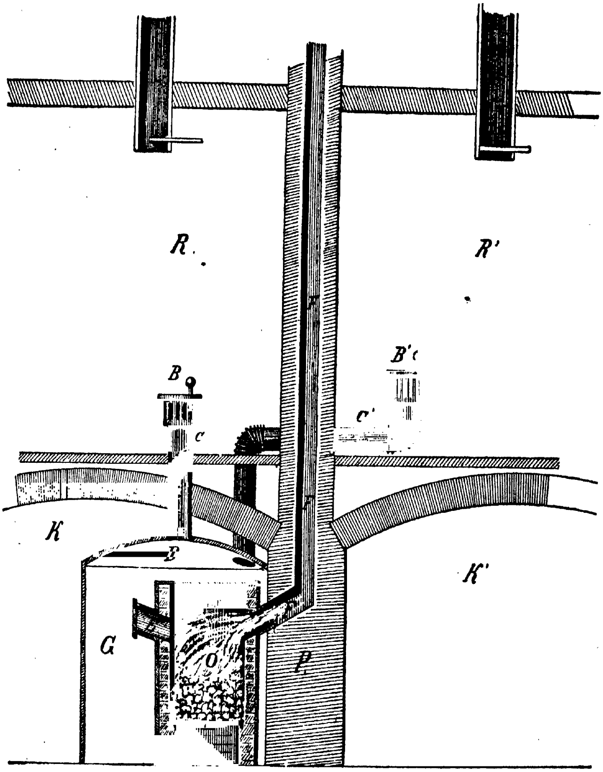
FIG. 32.



It is thus evident that both systems of heating have their advantages and defects, and the only question is how the latter may best be avoided according to the locality and circumstances of the establishment. General experience is the only reliable guide, and this, for reasons aforesaid, is chiefly in favour of heating with direct fire, if circumstances permit. Should, for any reason, this system be impracticable, then steam heating may be adopted as the alternative.

Fig. 33 represents a very simple heating arrangement with direct fire that is very convenient for the purpose in view. It is designed to serve for two drying-rooms. The rooms marked in the sketch by *R* and *R'*, represent the two drying-rooms, situated directly above the cellars, *K* and *K'*. One of these latter rooms contains the coke furnace, *O*, surrounded by an iron casing. The furnace, *O*, is made of very strong sheet iron, and is lined with fire bricks. The opening, *E*, which can be closed by a sheet iron cap when required, serves for charging the furnace with fuel. The smoke and gas from the fire-escape will be led into the flue, *F*, through the opening opposite.

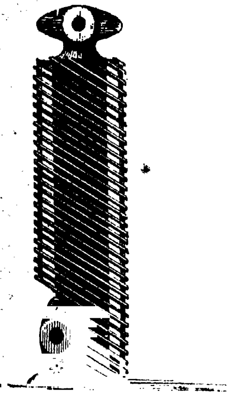
Fig. 33.



When the furnace is started, the air inside the casing, *G*, grows hot and rises through the pipes, *CC'*, in the roof, *D*, of the casing, *G*, into the drying-rooms, *R* and *R'*. This goes on uninterruptedly, since the air in the casing is continually renewed. The air pipes, *CC'*, also of strong sheet iron, are topped by adjustable cowls, *BB'*, by turning which the admission of hot air into the drying-rooms can be regulated as required.

The necessary ventilation of the drying-rooms is most suitably effected at the middle of the ceiling, as shown in Fig. 33. The spent, moisture-laden air is drawn off through iron or wooden pipes, provided at the lower end with suitable and easily adjustable dampers. If looked after with anything like care, the above described drying-apparatus will act perfectly, more especially for drying chromes, chrome greens, Bremen blue, &c.

FIG. 34.



When high-pressure steam is used as a source of heat for "drying-stoves," it must be conducted through a system of pipes, placed about 20 inches above the floor of the room containing the drying-racks. These pipes are provided with a number of gills so as to furnish a large surface and thus secure better radiation of the heat, as shown in the sketch (Fig. 34). The radiators are supplied by the makers in various shapes and sizes, suitable for every room, so that the fitting up of such a drying-room can be done by any skilled mechanic. To give some idea of the arrangement, a plan of such a "drying-stove," with steam radiators, is shown in Fig. 35.

In this plan, *RRR* signify the radiators, which in this case are straight, and are connected together partly by the steam pipe, *DD*, partly direct by bolting together their own flange connections. The steam (preferably direct) for heating the room enters at *A*, and can be conducted to either side by the valves *V* and *W* as desired. In both cases the steam escapes from the room at *B*, into a condenser, unless required for heating another room.

To secure an easy outflow for the water of condensation, it is advisable to give the whole series of radiators a gentle slope from *A* down to steam outlet at *B*, the radiators at *A* being highest and those at *B* lowest.

Of course all connections traversed by the steam must be most carefully packed with solid and durable packing, so as to prevent any escape of steam into the drying-room, since this escape of steam would be very inconvenient in the case of certain colours, to say nothing of the delay it would cause to the drying process itself. The other arrangements necessary for an efficient drying-stove, such as ventilation, air, light, walls, &c., are identical with those in hot-air drying, as already described.

Efficient ventilation is the most important factor in all "drying-stoves." Given proper ventilation, every kind of damp material can be dried, or at least made air-dry, in a room that is only slightly heated, if at all, but if that condition be unfulfilled, drying cannot be carried out properly even in superheated rooms. If the natural flow of air does not give sufficient ventilation, it must be supplemented by artificial means, such as exhausts, which draw the air out of the drying-room, or compressors, which force air into it.

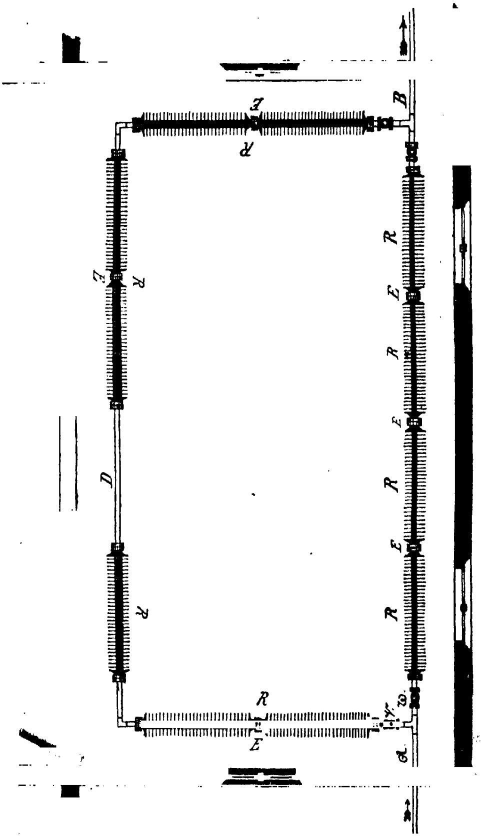


FIG. 35.

Latterly more complicated arrangements have been used to accelerate the process of drying. For instance, drying-kilns have been made in the form of a table of cast-iron plates. Steam-pipes, cast in the plates, are connected together, and traversed by steam from a boiler. These pipes heat the drying-plates, upon which the material to be dried is spread, and also heat the fresh air entering from below. Above the kiln is mounted a chest fitted with upcast flues. Several small kilns, arranged in a chest or barrel casing, form a drying-cupboard, which can be provided with circulating air and with devices for attenuating the internal air; in this latter case we have a vacuum drying-cupboard. The maintenance of a certain regular temperature, and the regulation of the flow of air, made possible by these devices, are very important in the case of valuable products.

Mention should also be made of revolving drying-cylinders, in which the material to be dried is moved forward by an endless screw. By properly adjusting the apparatus, the material entering in a moist state at one end will be discharged dry at the other end.

In large works drying-flues are sometimes employed with success. These flues resemble large tunnels, and are fitted with rail tracks for trucks carrying the laden drying-frames. A number of these small trucks are run into the tunnel and moved slowly onward. From the opposite end of the tunnel—the point where the trucks issue from it—heated air is introduced and circulates round the trucks, thereby gradually extracting the moisture from the material to be dried. As the trucks reach the hotter parts of the tunnel their contents are subjected to progressively higher temperatures, and finally the moisture is so completely extracted by the hot, dry air that the product arrives at the outlet as a perfectly dry powder. In large works the drying process can be effected in this way very quickly, and far more conveniently, than in a stove, whilst the higher first cost will be more than recouped by the saving in time and the simplification of the work. Of course it is essential that the output of the works should be large enough to keep the flue in constant work all day, and that the colours should stand quick drying without loss of brilliancy.

Grinding the Dried Colours

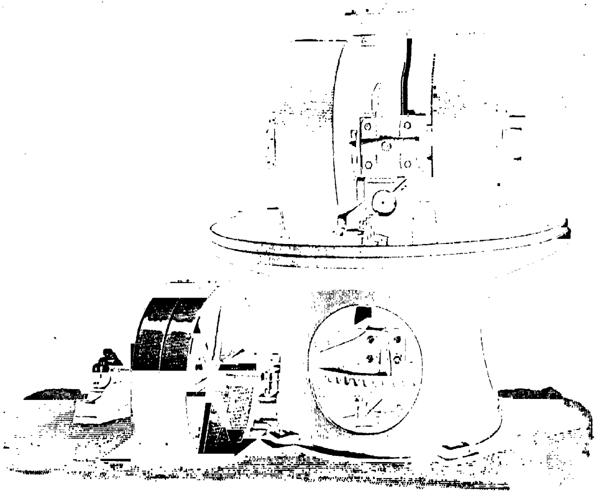
The dry colours are now sold in the form of a fine powder, this being the best for most purposes, and since the fineness of the powder depends on the method of applying the colours, the conversion into this form is a very important part of the manufacturing process. The solution of this problem is by no means simple, and the difficulties are increased by the fact that many industries using colours require—in order to turn out products capable of meeting competition—the powdered colours with the highest degree of fineness attainable, whilst, on the other hand, many colours, on account of their physical or chemical peculiarities, are very difficult to grind down to an impalpable powder. It would be erroneous to suppose that one and the same crushing machine would produce equally perfect results with all colours. While some colours are much too greasy or argillaceous to grind or sift with the ordinary crushing-machines, others, again, lose much of their brilliant appearance in the operation, and become dull and poor in shade. Others are so hard as to injuriously affect the grinding-machines, and suffer damage themselves from the heat generated by the friction. Hence several important factors have to be considered in the grinding of colours, a fact that is most in evidence when the colours are being made to match a sample. In fact, the selection of a grinding-machine out of the large number of types now available not only requires a proper knowledge and correct judgment of colours and their manifold qualities, but also a very extensive experience with regard to the efficiency and action of the innumerable machines recommended by the various makers. Grinding-machines for dry colours may be divided into four groups, viz.:

I. Preparatory machines for roughly crushing the colours (edge-runners, stamps, cone-mills, &c.).

II. Machines for grinding the crushed material to fine powder (grinding-mills).

III. Sifting-machines (screens, jiggers, &c.).

FIG. 36.



IV. Machines combining two or more of these operations (ball-mills or edge-runners, fitted with screens).

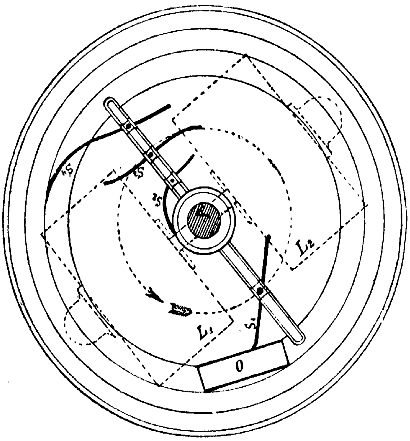
Most of these machines can also be used for more or less perfectly mixing two or more colours, whether the latter be already in the form of powder or in larger fragments. This oft-repeated and therefore very important operation will be described later on, it being first of all necessary to obtain a knowledge of the construction and practical use of the machines themselves.

Crushing-Machines

I. *Edge-runners*

It is impossible to mention all the different constructions of thes highly productive machines, and therefore only two varieties will now b. fully described, in order to give a sufficient insight into their methods of working. The principle of these mills is that of a pair of circular stones or runners, set edgeways, and running in a circular dished trough in which the material to be ground is placed. In some forms the trough is made to revolve, while the runners are made to turn on fixed centres or axes by the rolling friction of their edges on the bed of the trough, whilst in other forms the bed is fixed and the runners rotate on a movable central shaft. The stones are either of solid cast iron, or with jointed grinding rings of cast steel or chilled cast steel, ordinary millstones being also used.

FIG. 37.



The bed-plates are made of cast iron, steel, or chilled castings, or of granite, according to the material of the runners.

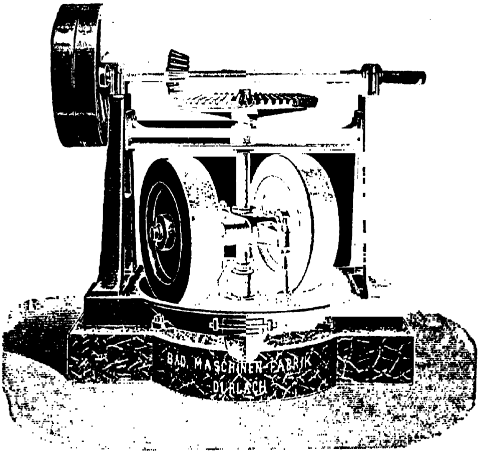
For colour-makers' use edge-runners made of stone are decidedly preferable to those made of any other material. In this type the lower millstone, forming the plate, is provided with a fairly high collar of iron, so as to enable as large a quantity as possible of material to be treated at a time. An opening, closed with a slide, is left in this collar, and communicates with a spout through which the colour, when sufficiently ground, is discharged by a scraper into a vessel underneath. The vertical driving-shaft of the mill is connected with two strong square iron bars between the runners, forming the axes of the runners, and mounted about twelve inches above the bottom stone. The cross-bars carry scrapers provided with a vertical and horizontal movement and travelling quite close to the bottom stone. These scrapers loosen the crushed and compressed colour, and return the same into the path of the runners (Fig. 37).

In practice a distinction is made between edge-runners with top and bottom drive. The first type is preferred for many reasons. The short vertical main shaft enables a hood to be fixed on the collar in such a manner as to cover the whole apparatus, thus preventing the operators from being inconvenienced by dust. Furthermore, in bottom driving the pulleys, cogwheels, and the connecting horizontal shaft are more firmly mounted in a secure foundation, an arrangement ensuring quiet running, and therefore a considerable reduction of wear and tear.

In top driving (Fig. 38), the pulley and countershaft must be fixed either on the ceiling of the room by means of hanging bearings, or must be mounted upon two strong supports (Fig. 38). The first arrangement is too unstable, owing to the weight of the whole apparatus, whilst the alternative method unduly restricts the space essential for security and comfort. These two reasons should in themselves be sufficient to give the preference to edge-runners driven from below.

Edge runners with rotating plates have recently been constructed, but have not fulfilled expectation as regards the increased output obtainable by their use. Apart from the more complicated mechanism, these mills do not show any superiority—at least for colour-making—over the ordinary edge-runners, and there is, therefore, no reason to employ such complicated machines when the same work can be performed by machines of simpler type.

FIG. 38.



II. *Centrifugal Mills or Disintegrators*

These consist of two or more concentrically mounted plates or drums (cages) of wrought iron, carrying on their periphery a number of steel rods or pins, and revolving at high speed in opposite directions. This motion is produced by two separate strong shafts carrying the drums and provided with ring lubricators. Since the rows of pins on the one drum cross between those of the other, the materials fed in from the centre are flung with great violence by the centrifugal force from one row to the next in opposite directions, and crushed. A readily detachable casing of sheet metal collects the materials that are expelled in the form of powder, and delivers them into a receptacle (Fig. 39).

In larger disintegrators the cages can be taken apart for repairing or cleaning (Fig. 40). The materials will be shovelled into the hopper of the machine in lumps or nuts not more than 1½ inches in diameter. Disintegrators have a high productive capacity, at least so far as quantity is concerned, and are also capable of reducing clayey materials to fine powder in a short time.

FIG. 39.

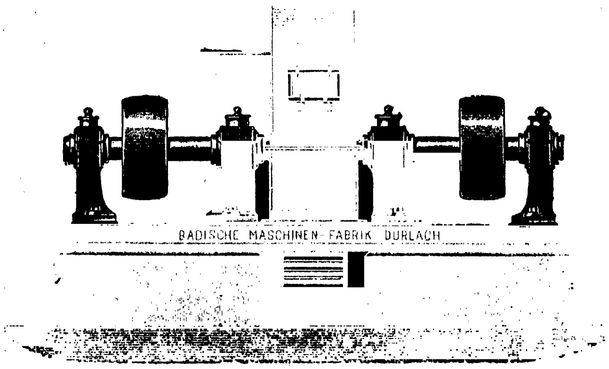


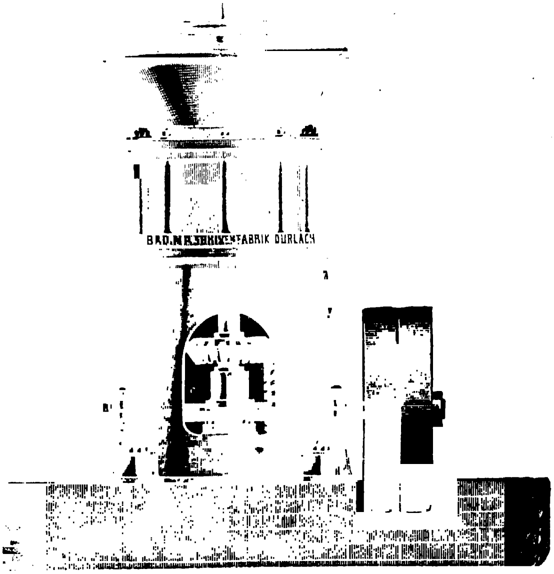
FIG. 40.

III. *Cone- or Bell-Mills* (Fig. 41)

Whilst the edge-runner machines and disintegrators are always used when dealing with large quantities, the cone- or bell-mills are only employed when small quantities of materials have to be reduced to powder.

These mills consist principally of a revolving cone and a fixed grinding-ring. The two cones are of different pitch, so that an annular space tapering downward is left between them. The grinding-cone and ring, or casing, are fluted, the flutings being coarser at the top and finer below, where the actual grinding takes place. The lower parts of the cone and ring are made of very hard castings, and being exposed to the greatest wear, are made easily exchangeable. The grinding-cone can be set to produce the desired fineness

FIG. 41.



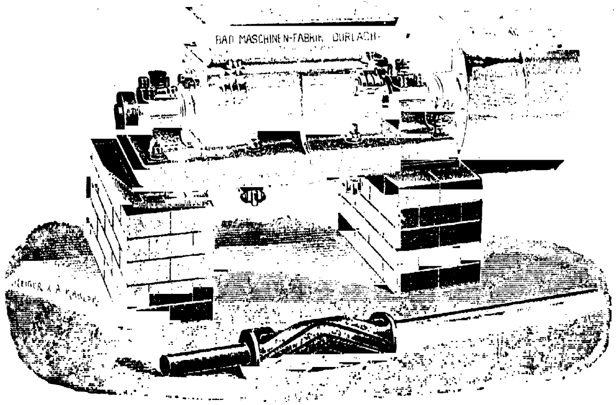
by means of a screw and without stopping the machine. The ground material falls into a gutter, from whence it is carried round to the discharge opening by scrapers, and is thrown out through the spout. These mills may be worked by hand or power, and are made of very high quality by the Badische Engine Works at Durlach as a speciality.

IV. *Screw Mills* (Fig. 42)

These belong to the class of roller mills, and are suitable for crushing both soft and hard materials. They consist of a strong casing lined with removable chilled cast plates. Connected with the casing is a grating of steel bars, which can be adjusted relatively at pleasure by lever and setting screws. Above this grating is a chilled roller provided with worm-gear grooved and run at high speed, so that the materials to be crushed are flung against the grating and broken. The pulverised materials fall through between the bars into a vessel placed underneath.

The main shaft of the grating is provided with a fixed and loose pulley, and can be driven direct from shafting. The whole apparatus takes very little room and requires but little power, whilst for certain colours its capacity is very high. Nevertheless, the resulting powder is by no means very fine, but needs further crushing in other machines.

FIG. 42.



We may now pass to the discussion of machines that furnish the best results in grinding colours to very fine powder, taking first, as being in the front rank, the mills in which the grinding is effected between two circular stones, one of which has a rotary motion.

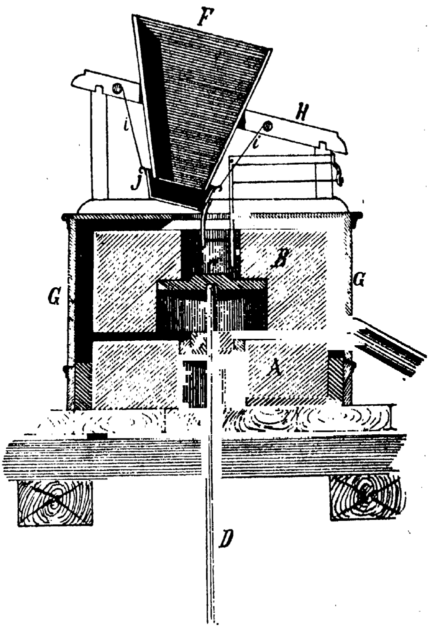
Fine Grinding-Machines

I. *Horizontal Stones* (Fig. 43)

An ordinary machine of this class comprises two stones—a fixed nether stone *A* and a rotary upper or grinding stone *B*. By means of a crosshead *C* the upper stone is supported by a vertical shaft or spindle *D*. This shaft passes through an opening or eye in the lower stone, and transmits motion to the grinding-stone. The spindle is packed by a box *E*. The material to be ground is fed from the hopper *F* through a central feed opening in the upper stone, and falls on to the lower stone, whence it passes in between the grinding surfaces and is ground. On reaching the outer edge of the stones it escapes as a fine powder into the casing *G* surrounding the stones, and is discharged through a shoot into a vessel below. The hopper *F* rests in a movable guide frame *H*. Underneath the mill hopper is a jigger *J* hung on four leather thongs *i i*, and shaken to and fro, to regulate the feed from the hopper, by means of a pin which is struck by projections in the feed opening of the upper stone. By raising or lowering the jigger the rate of speed can be accurately regulated by the thongs *i i*.

This, the oldest type of mill, is only referred to here in order to acquaint the beginner with the chief parts of these mills. In modern mill practice this type has been improved upon in a manner that leaves nothing to be desired as far as output is concerned. In particular, the use of iron as the structural material for these mills facilitates increased accuracy in setting, renders the parts easier of access, and lightens supervision. Fig. 44 shows such a mill of the latest pattern. The runner *B* rests by means of the crosspiece *H* on the spindle *M*, which is guided by the stone box of the lower stone *A*, the collar bearing *C*, and the footstep bearing *F*. This ensures the steady and safe running of the spindle, and consequently of the runner too. The footstep bearing rests on the screw *G*, the nut of which is formed by the hub of the pinion *R*, so that a slight turn of the latter enables the stone to be adjusted to a nicety.

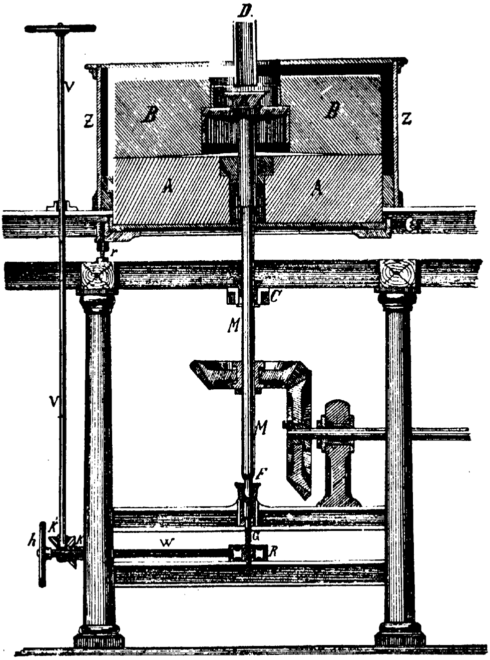
Fig. 43.



To enable this adjustment to be controlled from the casing *Z* as well as from the base of the apparatus, the shaft *W* carries, on its end nearest the spindle, an endless worm, engaging with the teeth of the wheel *R*, so that every movement produced by turning the hand-wheel *h* is transmitted to the spindle. The same movement, however, can be produced by means of two cone-wheels *K* and *K′*, the first being fixed on the shaft *W*, the other on the end of the vertical shaft *V*. By means of this train of bevel gear the motion imparted to the shaft *W* at *h* is transmitted to the spindle *M* and grindstone *B*. The crosspiece *H* is fitted at the top with a flat circular disc which in rotating distributes the material to be ground. The latter is fed through a regulating slide from the hopper *D*, and, under the influence of centrifugal force, is distributed evenly to the grinding surfaces of the stones. The lower stone is mounted, perfectly level and accurately centred, on three vertical screws *r r* traversing a strong iron plate, whilst on the other hand it is accurately centred by three horizontal screws *S S*, which pass through the turned-up edge of the flat circular iron plate.

The stones are driven either from a horizontal pulley keyed on to the spindle directly, or from a horizontal shaft and bevel wheels, the latter arrangement being preferable.

FIG. 44.



Having now more closely considered the principle of the mill, we can proceed to deal with the two chief varieties of this crushing-machine.

The mills with horizontal stones are divided into two classes, as follows:

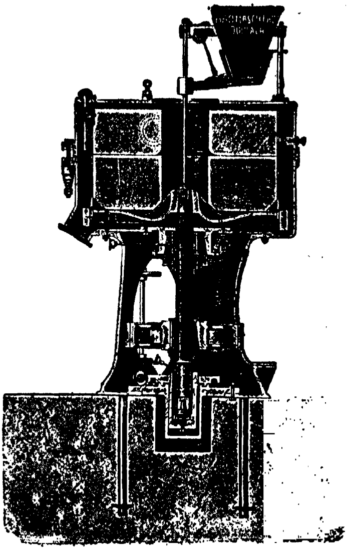
a. With fixed, but vertically adjustable, top stone and a revolving lower stone (Fig. 45).

b. With fixed, but vertically adjustable, lower stone, the revolving top stone being loosely mounted on the spindle. In another variety, now out of use, the under millstone was not adjustable, the grinding being regulated by raising and lowering the rotating upper stone.

The mills with movable lower stones are a modern improvement, and possess several important advantages over the second class. In the first place, the grinding pressure can be increased as desired. Furthermore, the material delivered by the hopper is fed directly on to the rotating lower stone, which distributes it and causes it to pass more rapidly between the stones than is the case with a rotary upper stone. Hence, whilst grinding the material equally fine, an increased quantity can be dealt with in the same space of time.

Both classes of mills are now supplied in a finished condition by the manufacturers, and are strongly built of iron except for the stones. In the mills supplied by the Badische Maschinenfabrik of Durlach the large circular bed-plate is firmly fixed to a brick foundation so as to prevent any vibration. The body is centred exactly on the hollow cast bed-frame by means of turned flanges, and the box of the collar bearing is bolted centrally in the bottom of this body in a similar manner. The collar bearing is in three parts, and the metal bushes are tightened centrally on the mill spindle, thus preventing the latter from shifting. In the same manner the box of the step-bearing for the spindle is fixed in the bottom of the hollow bed-frame, the casing of this bearing being centred and kept upright by means of a worm and pinion. By this means the spindle is prevented from jamming in its bearings when the mill is adjusted, and consequently the stones can be set extremely close without touching each other, thus preventing sparks. The bearing is lubricated at easily accessible places by means of solid grease, which keeps out dust and dirt. The conical or spur pinion is connected with the spindle by means of a clutch coupling which can be easily loosened when the wheel requires shifting. The crosshead at the top of the spindle is cemented to the lower stone and fitted very carefully, and is also screwed to the shaft of the hopper. At the circumference this crosshead carries scrapers for delivering the ground material to the spout of the mill.

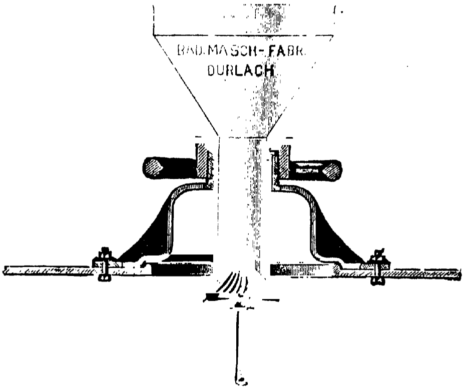
FIG. 45.



The edges of the body and hood, in which the upper stone is firmly but adjustably suspended, are turned to fit dust-tight, and are held together by bolts provided with flat coiled springs between the flange and the nut. These coiled springs give way when any hard foreign substance gets between the stones, and prevent the breakage that would otherwise result in consequence of the fixed relative position of the stones. A uniform feed is ensured by an adjustable centrifugal or jigging hopper, the former being regulated by a hand-wheel (Fig. 46).

In top-runner mills the construction of the several parts is the same

FIG. 46.



as described above, except that the grinding pressure is produced by the weight of the rotating upper stone, whilst the adjustment is effected by means of the lower stone.

II. *Excelsior Mills* (Figs. 47–49)

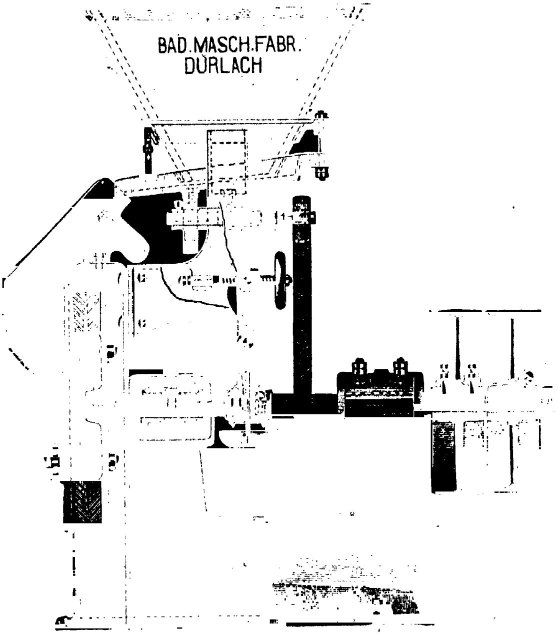
About thirty years ago there was introduced under this name a class of crushing-machine which has become widely appreciated on account of its suitability for a variety of purposes. Though simple in principle and having relatively small grinding surfaces, these mills have a high capacity in the case of a large number of colours, and since they take up little room, the reason for their popularity with colour-makers is evident. The working parts of the Excelsior mills consist of two rings (or discs), one fixed, the other rotating at a high speed, and both provided with a peculiar arrangement of teeth. The concentric rows of teeth of the one ring run between those of the other, and the material to be ground is fed into the middle by a vibrating hopper. The grinding discs are generally toothed on both sides, so that when one side is worn the disc can be reversed on the shaft.

Since the front edges of the teeth wear out first, the other side of the teeth can be utilised by reversing the direction of rotation by means of a crossed belt. The relative adjustment of the discs is effected by a set-screw. Fig. 47 shows the machine in cross-section, Fig. 48 a perspective view when open, and Fig. 49 the two grinding rings.

Sifting-Machines

The colours after being pulverised in a crushing-machine must usually be sifted to obtain the highest possible degree of fineness, or at least uniformity, of grain by eliminating the coarser particles. Here again a careful differentiation must be made between the large number of forms available, according to the kind or quantity of the colours to be sifted, since no one machine will give equally satisfactory results in all cases.

FIG. 47.



As every colourman knows, the sifting of colours is a somewhat difficult operation, entailing much trouble and often requiring a considerable expenditure of time and patience, and it is therefore not easy to give useful hints and advice in this matter to the beginner. Nevertheless, we will deal as fully as possible with the sifting appliances that have, according to general experience, behaved best in practice.

I. *Centrifugal Sifting-Machine*

This machine is met with in practice in a great variety of forms, all, however, based on the same principle—namely, that the material to be sifted is passed through a long round or hexagonal cylinder covered with some kind of metal or silk fabric. By means of a device fixed on a shaft run at high speed, the material is continually flung against the fabric, the finest particles of the powder being forced through the meshes of the screen, whilst the coarser particles are discharged at the open end of the cylinder. The fundamental idea of this method is an obvious one, and is embodied in the construction of many forms of sifting apparatus, especially those of earlier date. Naturally, however, these machines take up a very large amount of room, since the dimensions must be greater in proportion as more perfect sifting is required.

FIG. 48.

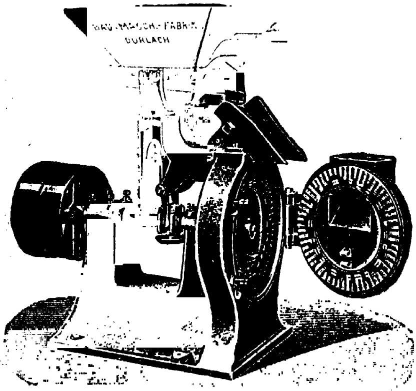
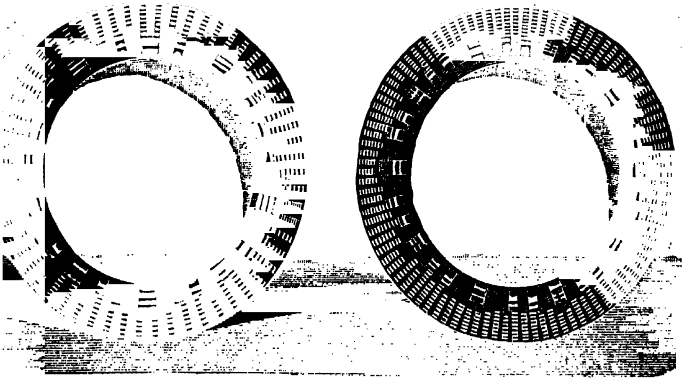


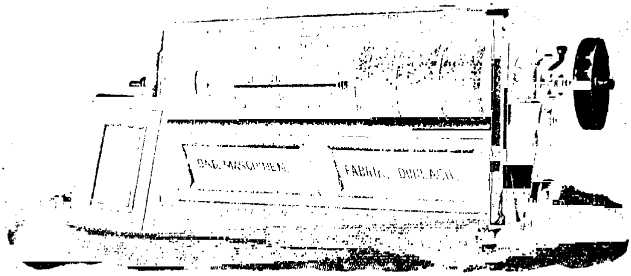
FIG. 49.



These large machines being always inconvenient, attention has been directed to guiding the materials to be sifted more frequently over the screening surface, thereby enabling the size of the cylinders to be reduced This problem has been easily and satisfactorily solved by the aid of bent centrifugal vanes running at very high speed on a common shaft.

In the apparatus represented in Fig. 50 the materials to be sifted are fed by a worm into the circular sifting-cylinder, fitted inside with centrifugal vanes of special shape. These distribute the powder equally over the whole surface of the sifting-cylinder, and at the same time move it onward in the direction of the shaft. The sifting frames of the cylinder are made of wood and covered inside with wire or silk gauze. These frames are fastened by wing screws on to the ribs of the cylinder, and can therefore be quickly and easily changed. The sifted material falls into the lower conical part of the apparatus, whence it is removed by the aid of a worm. Though in most centrifugal sifting-machines the sifting-cylinder is fixed, in some types it is rotary and moves in the opposite direction to the vanes. This arrangement, of course, involves a very complicated system of pinions, gearing, &c., which makes the apparatus more expensive without correspondingly increasing its productive capacity. (See Fig 62.)

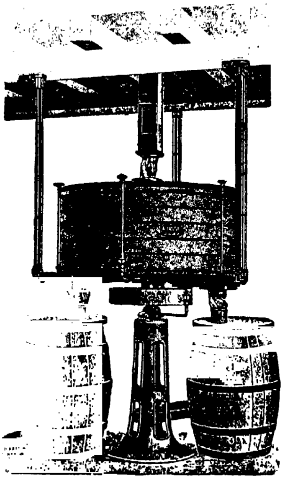
FIG. 50.



II. *The Jasse Sifting-Machine* (Fig. 51)

This sifter consists of two or more superimposed circular screens, the number being suitably increased or lessened according to the capacity or the class of product desired. The material to be sifted is introduced through a central hopper, and falls on to a disc which distributes it equally over all parts of the sifting surface. The rotary motion of the sifter throws the material to and fro, just as in a hand sieve, until, driven onward by other portions behind, it falls over the outer edge of the sieve. It thus reaches the second sieve, where the same treatment is repeated, except that the direction of movement is now from the outside to the centre, where it falls through the middle and on to the next sieve. If there are only two sieves, the material then drops to the bottom of the sifter, and being conducted to the outside, is collected in a sack or a barrel placed underneath. The powder that has passed through the sifting-gauze also falls on to a collector underneath each sieve, and is conveyed outward for removal. The gauze is kept perfectly clean by a very simple arrangement, which does not touch the gauze at all, so that the premature wearing of the gauze is completely avoided.

FIG. 51.



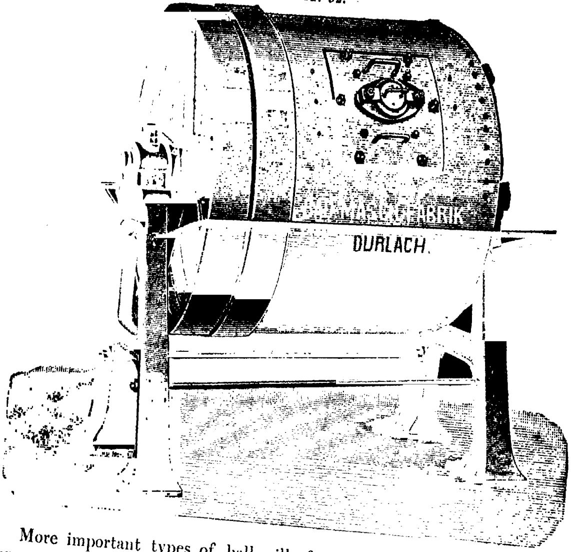
The construction of these sifters is based on the principle of a plain natural sifting of the powdered materials in the same way as by an ordinary hand sieve. Since there is no violent impact of the material against the sifting surface, no coarse particles are forced through the meshes of the sieve, and the results will be exactly uniform under all circumstances. With regard to the productive capacity, the Jasse machine is in many cases superior to other types, one reason being that the whole sifting surface is utilised, and another that there is no need for such close fabrics as must be used in centrifugal machines. The apparatus takes up only a very small space, and works absolutely dustless; another point in its favour, so far as a number of colours are concerned, is that the power consumption is very small in comparison with some other machines. Finally, it may be mentioned that the great ease with which the sieves can be changed enables the product to be altered in a short time without any detrimental consequences to the shade of the colours.

Drum or Ball Mills (Figs. 52–54)

In these mills the crushing of the material is effected by a number of forged, very hard steel balls of different sizes, which are kept rolling by slowly rotating the drum, and thus gradually crush the material introduced between them. According to the nature of the colours, a distinction is drawn between ball mills fitted with sifting devices and the simpler forms (Figs. 52 and 53) in which the drum, on being charged, is closed, then kept revolving for a long time, the actual duration depending on the character of the material under treatment.

To empty the mill the cover is removed and a grid inserted in the opening, the drum being then started again. On account of the very large amount of dust given off during this operation, the drum must be enclosed in a dust-box fitted with a discharging shoot and sliding cover. The ball mill illustrated in Figs. 52 and 53 can only be used when a uniformly ground product is not essential; otherwise this latter must be sifted after it leaves the drum.

FIG. 52.



More important types of ball-mills for colour-makers are those fitted for screening and discharging the ground material continuously (Figs. 54 and 55).

FIG. 53.

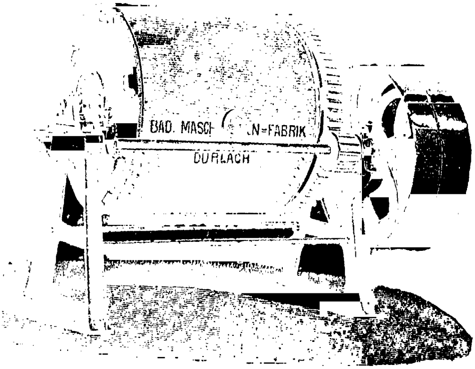
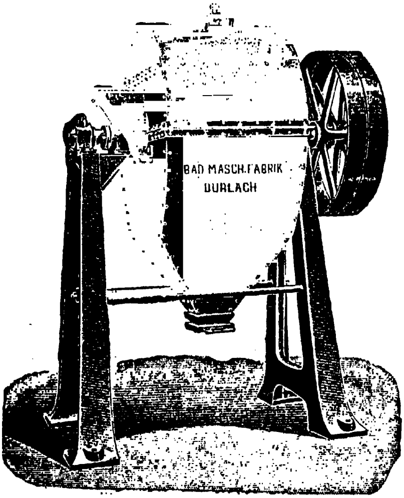


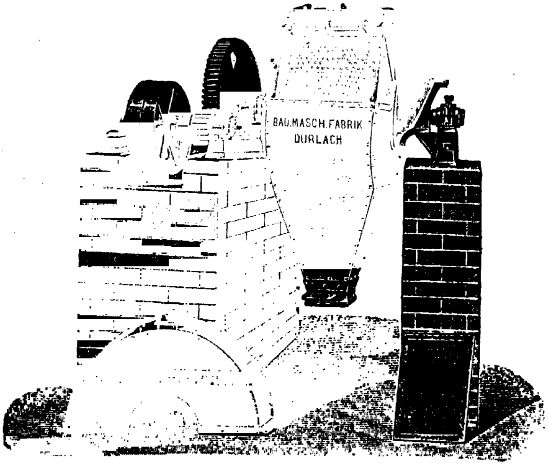
FIG. 54.



In these mills which, as already mentioned, also effect the rough crushing of the material, the grinding drum proper consists of two strong side-plates, one of which is provided with a removable arm and also serves as a feed-hopper.

Both side-plates are protected internally against wear by hard cast plates which can be easily changed. The grinding surface itself is formed of heavy reversible rolled steel grinding beams, and by cast steel back-throw beams, with intermediate adjustable slits, through which the crushed material escapes from the drum. This grinding surface is surrounded at a short distance by detachable protective screens, and these in turn by the detachable fine sifting-frames. The material crushed by the slits in the grinding surface first encounters the protective screens, and from

FIG. 55.



these it reaches the fine screens. Such of the material as will pass through the meshes of the fine sieves thereupon leaves the mill, whilst the coarser portions fall back upon the back-throw plates and into the inside when the drum reaches a suitable position. The material in these mills also is crushed by balls of different sizes. The whole of the grinding drum is surrounded by a tight-fitting dust-box fitted on the top with a ventilating pipe, to which a dust exhaust pipe can be connected. At the bottom of the dust box is a discharge pipe, with sliding cover, for drawing off the ground material. The mill must always be run in the direction and at the speed prescribed in the instructions, and should be kept filled with sufficient material to prevent the balls from striking directly against the grinding beams for any length of time. When the mill is being under-fed the balls give out a characteristic metallic sound.

General Notions about Properties and Applicability of Colours

Whilst the detailed characterisation of the various colouring matters and pigments must be postponed until we come to deal with them separately, some general introductory remarks may now be given as facilitating comprehension of the references that will then be made in the text.

The choice of a colour for colouring any given article is by no means a matter of indifference. It is not sufficient that a certain colour appears to have a suitable shade and tint, but in addition that the total chemical and physical properties of the colour must be suitable for the purpose, the method of application, and the local conditions, as well as the influences which the material itself exercises or to which it has to be exposed. That is to say, the colouring-material must be able to form with the coloured one a combination which must be durable and capable of withstanding all outside influences in a high degree.

With regard to the external influences acting on all coloured objects, the chief of these are the light and the atmosphere, whose chemical influences have also to be considered. Photography demonstrates the chemical activity of light; and since on the one hand in photography we utilise the decomposing effect of sunlight upon silver salts, we must on the other put up with the fact that this same sunlight exerts a similar influence in other directions, namely, compounds having a certain value as colouring matters. Therefore where the protracted influence of light upon an object has to be reckoned with, a colour that is fast to light must be taken. It must be mentioned that this chemical activity is not confined to bright, direct sunlight, but is also possessed by diffuse daylight, though in a less degree.

First among the colours that are not fast to light are those of the organic group, comprising not merely the majority of coal-tar colours and their lakes, but also the colours obtained from plants, though not without exception, natural and artificial indigo, natural madder and the artificial (alizarine lake) being, for instance, very fast to light. Inorganic colours are generally fast to light, but some, especially such white colours as lithopone, are affected by prolonged exposure to light.

In addition to light, the small quantities of gaseous impurities present in the air also have a destructive effect on delicate colours. For instance, the air close to gas-works or to large industrial furnaces, manure heaps, &c., will contain a certain amount of gaseous sulphur compounds—ammonium sulphide, sulpho-cyanogen, carbon disulphide, &c.—formed as products of the combustion of coal or of the decomposition of organic bodies containing sulphur and nitrogen escaping into the open air. Where such gaseous contamination exists, no colours may be used that contain ingredients sensitive to sulphur. These comprise all compounds containing lead, for instance, white lead and chromes, these turning colour in consequence of the formation of black sulphide of lead.

In the neighbourhood of chemical works the air often contains acid vapours, such as nitrous or nitric acid, sulphurous acid, chlorine, &c., which have a very strong decomposing action and are rapidly destructive of colours with a low resisting power. Solar heat, a damp air, rain and snow accelerate the process of decomposition. The small quantities of nitric acid and ammonia always present even in pure country air may also exert an influence on sensitive colours.

The fact that genuine vermilion is not a fast colour, but turns brown in air and light, and finally becomes quite black, is apparently due to a physical process resulting from chemical action. The altered vermilion has still the same chemical composition that it had before as a red colour, but the physical structure is different; it is probably due to an amorphous modification. (*See* the manufacture of genuine vermilion.) Objects (for instance, prints) coloured with vermilion are more permanent in colour when protected against light and air. Some colours are capable of being restored after having suffered by influence of light by their being kept for some time in the dark, or *vice versâ*, as is the case, for instance, with white lead, which in the state of oil paint quickly turns yellow in the dark, but becomes quite white again on being exposed to the light for some time.

The destructive influence of acids has been mentioned already, and a still more important influence in many cases is the decomposition effected by alkaline substances, especially where the colouring of bodies with an alkaline reaction is in question. This is the case where a lime-plastered house has to be painted, or where the colour is added direct to the lime plaster, as is done in decorative painting and in fresco work. In such cases, therefore, colours that are fast to lime must be used.

It often happens that painted objects, or such as have been coated with colour by printing or hand-work, are covered with a layer of lacquer varnish (*i.e.*, solution of resin in oil or spirit) in order to improve the brightness of the colours and protect them at the same time. In this connection it must be remarked that for more valuable works of this kind it is sometimes the practice to use colours which, though distinguished by their vividness, brilliancy and variety of tint, are not always capable of resisting the solvent action of the spirituous solvents present in the resin varnish. The result is that the colours themselves pass into solution too, and consequently the entire painting may be endangered. Hence, objects that are to be varnished afterwards must be painted or printed solely with colours that are insoluble in varnish; and in addition these colours must be thoroughly dry before the varnish is applied. All inorganic colours are fast to varnish; but many, and especially the most brilliant, organic (coal tar) colours are not so.

The earthenware and porcelain table ware in daily use is decorated with coloured designs and other coloured ornamentation; and these articles, as we know, have been fired in the making, being exposed to a very high temperature in that process. Hence for ceramic purposes only fireproof colours are suitable; and these, though they do exist, are very few in number. They are, of course, exclusively of inorganic origin, being generally metallic oxides, such as are also used for enamels and glaze colours.

The manner in which the colouring matter is fixed on the material to be coloured is variable. In painting, the colour is finely diffused in a liquid substance, the vehicle (size, varnish), and then applied to the object in a suitable manner. The vehicle in which the colouring matter is disseminated dries gradually on the painted article, and then adheres to the latter, which consequently is not stained itself, but is merely coated with colour. The process of dyeing is quite different, the whole mass in this case being stained right through. In making coloured paper, the colouring matter must be added to the paper stock at the beginning of the manufacturing process, and consequently no special fixing medium is required. The colour added may consist of a finely distributed solid pigment (for instance, ultramarine), or of an aqueous solution of some organic colouring matter. In dyeing cloth the latter process is generally used—*i.e.*, an aqueous solution of the colouring matter is employed, the colouring matter being precipitated or developed upon the fibre in a suitable manner. It appears, therefore, that for certain purposes solid pigments must be used, whereas in other cases colouring matters soluble in water are employed. Now all inorganic colours are insoluble in water, whilst most pure organic colouring matters are soluble therein. The latter, therefore, are more particularly used for dyeing, the former for painting.

In painting with colours on a white (*i.e.*, in the practical sense a colourless) surface, it is for the moment a matter of indifference whether the colouring material selected takes the form of a compact, heavy coat or a thin, transparent film. In both cases the colouring effect will show up clean on the pure white ground. It will, however, be quite different when the object to be coloured is already of some pronounced colour, or quite black, the coloured ground then needing to be coated with some more powerful colour. If in this case a slight and transparent colour were selected, it would be impossible to mask the ground colour, and the result would be a combination of optical effects, furnishing either a blend of the two colours or leaving the stronger colour of the ground predominant. Thus in the case of a light blue ground and the applied colour a transparent pale yellow, the resulting effect will be green. On the other hand, with a dark blue ground and a very light yellow applied colour, the colour effect will remain dark blue, the light transparent yellow being too weak to affect the result. In order to obtain a strong yellow effect by painting or printing on the dark blue ground, one must choose colours whose optical effect will be to destroy or mask that of the underlying colour. Such colours are known as *opaque colours*, the antithesis of these being *transparent colours*. The quality of opacity is not always inherent in the pigment itself, since a transparent colour can be rendered opaque by suitable additions. In the same way, an opaque pigment can be transformed into a transparent one by suitable additions, though with less success, and usually at the expense of the colouring power. A large number of inorganic colours are naturally opaque, though no strict line of demarcation can be drawn between the two classes, and many colours can be used as opaque or transparent colours according as they are laid on more compactly and thick, or lighter and thinner. The covering power of a pigment varies inversely with its crystalline character. The amorphous condition gives the best results in this respect, the specific gravity being immaterial. For instance, lamp-black may be mentioned as a specifically very light colour with a very high covering, and most intense colouring power. Further for instance, genuine vermilion, Krems white, chromes, &c., are in the pure state excellent covering pigments. Terra di Siena and Blanc fixe are intermediate between the opaque and transparent colours, and the pure alumina coal-tar lakes are decidedly transparent. To some extent also the quality of opacity or transparency is influenced by the medium, or vehicle, with which the pigment is mixed and laid on.

A whole series of artificially produced colours are also found ready formed in Nature. Thus, natural cinnabar and the artificially produced genuine vermilion, or again, natural lapis-lazuli and the artificial ultramarine, are chemically identical. As pigments, however, they are not practically equivalent, the artificial products being far preferable in this case, although the natural products are of greater money value on account of their rarity. The morphological structure of all natural mineral compounds is crystalline, and they cannot be reduced, even by repeated crushings and grindings, to such a fine state of division as that easily obtained in the production of the same compounds by suitable artificial means, which as a rule do not undergo any special crushing process. Hence, for colour purposes, the preference will always be given to the artificial products over such as are found native.

The vehicles used for grinding colours are generally divided into oleaginous (linseed oil, varnish, resin), and aqueous (gum, casein-size). All colours can be made up as oil or water colours, and the form in which they are treated for certain purposes depends mostly on practical considerations alone, and not on chemical or physical reasons. In most cases the pigment is suspended—or more rarely dissolved - in the vehicle unchanged; and in any event they must not react on each other in any way tending to result in the decomposition of one or both, thus destroying the colour and rendering the vehicle ineffective.

Some colours enter into chemical combinations with the oleaginous varnishes, thereby improving instead of impairing the properties of the paint. Thus the lead pigments combine with linseed oil varnish to form lead soaps. It is easy to comprehend that this chemical process of saponification gives the pigment greater homogeneity, and therefore better covering power, and higher adhesive capacity than is the case with a simple mechanical mixture. In other cases, however, the reverse sometimes occurs, colours mixed with size or starch, for example, undergoing acid fermentation in certain circumstances. When the colouring matter consists of certain delicate organic dye-stuffs or lakes, the highly disagreeable result in such event will be complete decomposition of the colouring matter and the conversion of the originally bright coloured workable pigment into a discoloured, malodorous liquid.

Finally, it should be mentioned that some colours will react on one another when mixed. For instance, lead colours are very sensitive to the influence of gases containing sulphur, and also to colours containing that element. For instance, white lead or chrome yellow must never be mixed with ultramarine or vermilion, both of which contain sulphur in a loosely combined form. This sulphur will combine with the lead more or less rapidly, according to circumstances, the reaction being favoured by the intimate contact of the pigment molecules in a homogeneous colour mixture, the operation of grinding and the process of mixing the pigment and vehicle, the latter being generally attended with a slight generation of heat. For instance, a mixture of ultramarine and Krems white would leave the mill not as a light blue, but as an already discoloured grey-blue, which soon turns into a dirty dark blue, and finally into black. Lead and copper colours are specially sensitive to sulphur, and therefore must not be mixed with ultramarine, vermilion, or lithopone.

The points mentioned here apply equally to artists' colours and industrial paints, the object being to give the beginner some general ideas enabling him to know and appreciate the factors and conditions which have to be considered in the proper compounding of colour mixtures and vehicles. As a matter of course the vessels and apparatus used in the preparation and storage of colours must be selected in accordance with the properties of the latter. Ultramarine and cinnabar vermilion, for instance, must not be ground with iron rollers, nor kept or treated in lead or copper vessels.

Having now dealt with the various properties of colours, a short description may be given of easy and rapid methods of testing colours for the possession, or otherwise, of certain of these properties.

The *fastness to light* can be tested by spreading the pigment, along with quick-drying linseed oil varnish or size, on a paper or cardboard surface, and allowing it to dry superficially. About one-half of the layer of colour is then covered tight with dark cardboard or paper, the sheet being fastened with drawing-pins, or similar means, on a board and exposed to the light in a suitable place, protected from the rain if out of doors or near a window indoors. Exposure to the direct sunlight is a drastic test, under which fugitive colours will show a remarkable change in the course of a day, sometimes even in a few hours. In diffused daylight the test naturally takes longer, but even in this case a week will generally be sufficient. On removing the protecting card, &c., from the covered part of the colour surface after the test is ended, no difference will be observable in the case of fast colours with regard to the shade of covered and exposed parts, though it may happen that the exposed part has suffered perhaps to some extent by dust or other influences. According as the colour is more or less sensitive to light, the exposed part will be found to be more or less faded.

Coincidently with the foregoing test, the colour may be tested for its ability to stand *climatic influences* by exposing it out of doors for a suitable length of time.

Fastness to alkalies is determined by well shaking up the dry or mixed colour repeatedly with milk of lime and a corresponding quantity of water, and leaving it to stand. If the colour is not fast to alkalies it will fade and decompose.

When a colour is to be tested as to its suitability for fresco painting, in which case it must also be able to resist the action of silicic acid, the same experiment is performed, but with cement instead of lime. For certain purposes (for instance, printing on tins used for preserves) the colour must be able to stand high temperatures, though usually not exceeding 212° Fahr. The test in this case is made by shaking the colour up with boiling water. After the colour has settled down in the glass, or has been filtered off, the water should be colourless or only very slightly tinged.

Ceramic colours must be able to stand considerably higher degrees of temperature—the temperature of the glost kiln—in addition to fulfilling certain other conditions which cannot be gone into here.

The *fastness of a colour to spirit* is determined by shaking up the dry or mixed colour with strong alcohol (60 per cent. at least), with or without warmth, as the case may be. If the alcohol remain colourless, the colour is fast to alcohol (spirit-proof). In this manner ochre and genuine vermilion, for instance, are tested for additions of coal-tar dyes to brighten them up. A colour which is not spirit-proof in the sense of the foregoing test may nevertheless be suitable for varnishing—*i.e.*, will stand coating with spirit lacquer without running, provided a linseed oil varnish has been used as the vehicle, and the painting or printing has become completely dry before varnishing. Colours — especially lakes made with coal-tar dyes — which are not too readily soluble in spirit will in such case remain completely unaffected, being enveloped in the dry varnish, whereas more easily soluble colours will run to a greater or smaller extent.

If a colour mixed with varnish be spread on a sheet of glass in such a way that a surface of about one square centimetre is covered evenly and not too thickly, and the glass be then placed on a printed sheet, such as a newspaper, the underlying print will not be discernible if an opaque colour has been used, though it will be visible in the case of a transparent colour. The intermediate stages here are very numerous, very many colours being neither purely opaque nor purely transparent, but approximating more or less in their properties to one category or the other.

To compare the colouring power of two or more colours, it is necessary to prepare a pure white colour mixed with varnish, and then add to each 100 parts of the white colour 1·2 parts of the dry colours to be tested, these samples being rubbed down in a porcelain mortar until perfectly homogeneous. The colour in the mixture that gives the deepest tinge will have the strongest colouring or tinctorial power. The same test may also be performed with dry white pigments—white lead or zinc white, blanc fixe being the best.

An injurious sulphur content in a colour of unknown composition can be detected by rubbing down the dry colour in water with Krems white, slightly warming it if necessary. The presence of sulphur will be revealed by the original pure light tone of the colour becoming a dirty grey-black, according to the amount of sulphur available to form lead sulphide.

To test the fineness of grinding, a certain quantity of the colour is placed in a small, loosely-tied bag of fine silk gauze, shaking the bag gently and dropping it upon a sheet of paper underneath so long as the gauze continues to allow any of the colour powder to fall through. When all the fine colour has been shaken out of the bag in this way, the coarse residue in the bag is determined by weighing. According to the degree of grinding or pulverisation employed, a correspondingly coarser or finer mesh gauze is used for the bag, the exact gauge of the gauze being ascertained by the number of meshes per unit area (*e.g.*, square inch).

The Nomenclature of the Colours

It is advisable to say a few words about the nomenclature of colours, although unfortunately no systematic classification has been adopted in this respect. On the contrary, the names of colours have been quite arbitrary, and not only manufacturers, but merchants too, think themselves entitled to fix the name of any kind of colour they are going to produce, or have mixed or compounded from others, or to which they have done nothing beyond undertaking the sale of the article—in some cases re-naming a well-known product in order to increase the sale by putting it forward under the guise of novelty. Such conduct is facilitated by the deplorable lack of technical knowledge among users of artists' and painters' colours; on this account the endeavours latterly made to increase that knowledge among consumers are a source of gratification.

Though we do not wish to imply that this confusion in the nomenclature of colours arises from dishonest motives, it cannot be denied, on the other hand, that the existing state of things is conducive to dishonesty in the colour-trade, and has, as a matter of fact, opened the door to malpractices. Indeed, there is at present no trade (especially in the retail business) where description of the goods is so unreliable as in the colour trade.

As stated, anybody considering it advantageous to do so claims the privilege of giving any name he pleases to a colour apart from its existing name, the result being that, on the one hand, a single colour is sold under several—indeed, sometimes a dozen—different names, whilst, on the other hand, one finds a single name applied to a whole series of different colours.

For instance: white lead (basic carbonate of lead) is also sold as Krems white, Dutch white, Venetian white, slate white, Berlin white, silver white, &c. Conversely, three entirely different colours are found in the trade under the name of Indian yellow. First of these is the perfectly pure, genuine Indian yellow, which is an animal secretion and is obtained from the urine of oxen, camels, and horses fed on the leaves and fruit of the mango in India. Another Indian yellow is a lake made from coal-tar dye; and finally a cobalt colour (potassium and cobalt nitrite) is called by the same name.

This clearly shows that in many cases the purchaser of colours who merely asks for a certain article by name is liable to get something different from what he really requires, it being evident that the colours which are actually different, though named alike, do not possess the same chemical and physical properties. Hence in all cases where a certain material of definite character is required it will be necessary, in order to be sure of getting the right article, to specify distinctly which properties the colour is required to possess. Apart from the great number of fancy names: Victoria green, new blue, patent red, Mars yellow, emperor green, royal blue, cœruleum, English red, &c., colours are often named after their inventor, Scheele green, Perkins's violet; after the original or principal place of origin, Berlin blue; after the place where they are found in nature, Terra di Siena; after their ingredients, chrome yellow, white lead; after their resemblance to some colour found in nature, turquoise-blue, sky-blue; after the purpose for which they are used, signal-red; after the raw material used in their production, vine-black, ebony-black, &c. In all these cases, however, one can never be sure that the article supplied under the same name by different manufacturers and dealers will be exactly the same product. In the comparatively new industry of coal-tar colouring matters and the colour lakes made therefrom a better state of things prevails, since the products are very often called by their full scientific name or abbreviations of the same, expressing their chemical composition. Where fancy names are applied for the sake of convenient brevity (eosin, lithol red, &c.), these generally relate to patented goods, the name being also protected by the patent. The ideal nomenclature in all cases is that expressing the chemical composition of the colours. This, however, would seem to be impracticable, at all events for the organic colouring matters, since in many cases their complex structure can only be explained by lengthy chemical formulæ and therefore by correspondingly long and perplexing scientific nomenclature, difficult to pronounce.

In commerce (*especially the retail trade*) one can never be sure that a colour sold under any given name is the same in all cases. To be on the safe side the buyer should specify exactly the properties which the required colour is expected to possess, which done, any honest and competent dealer will be able to supply what is wanted.

PART II

THE MANUFACTURE OF THE ARTIFICIAL MINERAL COLOURS

WHITE MINERAL COLOURS

Only a comparatively limited number of white mineral colours have any extensive technical application. The most important representatives of this group are:

1. *Blanc fixe* (also called permanent white, barytes white, fast white).
2. *Zinc White* (zinc oxide, flowers of zinc, snow white, &c.).
3. *White Lead* (Krems white, slate white, Berlin white, silver white, &c.)
4. *Lithopone* (zinc sulphide white).

This last-mentioned has recently gained such a prominent place on the market as a substitute for white lead that a number of large works have been specially equipped for its production.

I.—MANUFACTURE OF BLANC FIXE (*Artificial Barytes*)

According to its chemical composition, blanc fixe is pure barium sulphate with the chemical formula $BaSO_4$. It is manufactured in considerable quantities by precipitating a solution of barium chloride with sulphuric acid or cheap sulphates such as Glauber salt, magnesium sulphate, &c.

For the production of barium chloride, as the raw material for the manufacture of blanc fixe, two minerals are available, namely, the natural barium sulphate, known in commerce as barytes, and, secondly, barium carbonate (witherite), a mineral also found extensively in nature. This latter is far preferable to barytes, on account of its cheapness and relatively easy decomposition by the aid of hydrochloric acid.

To convert barytes (which is well known to be a compound extremely difficult to be reduced to the soluble form) it must first be treated by a very lengthy and troublesome process. This consists of calcining the finely pulverised barytes with a material rich in carbon, in which process the carbon combines with the oxygen of the barytes and reduces the latter into barium sulphide. The latter can then be decomposed with hydrochloric acid.

The chemical reaction occurring in the reduction of barytes to barium sulphide may be represented by the following simple equation:

$$\underbrace{BaSO_4}_{\text{Barytes}} + \underbrace{4\,C}_{\text{Carbon}} = \underbrace{BaS}_{\text{Barium sulphide}} + \underbrace{4\,CO}_{\text{Carbon monoxide,}}$$

the latter escaping as a gas.

In the next operation, the treatment of barium sulphide with hydrochloric acid, the products are barium chloride and sulphuretted hydrogen gas. Such considerable quantities of this gas are liberated that their removal by the means available in most colour manufactories is often attended with the greatest difficulty. In fact, the chief disadvantage in the method of producing barium chloride from natural barium sulphate as compared with witherite consists in the fact that, in the most favourable circumstances, the complete elimination of the sulphuretted hydrogen can never be successfully effected.

The decomposition of barium sulphide by hydrochloric acid into barium chloride and sulphuretted hydrogen proceeds in accordance with the following equation:

$$\underbrace{BaS}_{\text{Barium sulphide}} + \underbrace{2\,HCl}_{\text{Hydrochloric acid}} = \underbrace{BaCl_2}_{\text{Barium chloride}} + \underbrace{H_2S}_{\text{Sulphuretted hydrogen.}}$$

In the actual manufacture of blanc fixe, the barium chloride obtained as above must be treated with dilute sulphuric acid or with an aqueous solution of one of the above-mentioned sulphates, the barium sulphate being thrown down as a finely divided precipitate. When dilute sulphuric acid is used as the precipitant we obtain the products given in the following equation:

$$\underbrace{BaCl_2}_{\text{Barium chloride}} + \underbrace{H_2SO_4}_{\text{Sulphuric acid}} = \underbrace{BaSO_4}_{\text{Blanc fixe}} + \underbrace{2\,HCl}_{\text{Hydrochloric acid.}}$$

The two molecules of hydrochloric acid previously used for the decomposition of the barium sulphide are here recovered, and can be used over again for the same purpose, though, for two reasons, this is possible to only a certain extent. Thus, the hydrochloric acid becomes more and more dilute in repeated use, so that eventually it would cease to act at all. On the other hand, it would gradually absorb such a large quantity of the impurities contained in the barium sulphide as to become useless.

The precipitation of barium chloride by sulphates (Glauber salt, Na_2SO_4, or Epsom salt, $MgSO_4$) proceeds in accordance with the equations:

$$(1)\quad \underbrace{BaCl_2}_{\text{Barium chloride}} + \underbrace{Na_2SO_4}_{\text{Glauber salt}} = \underbrace{BaSO_4}_{\text{Blanc fixe}} + \underbrace{2NaCl}_{\text{Common salt,}}$$

$$(2)\quad \underbrace{BaCl_2}_{\text{Barium chloride}} + \underbrace{MgSO_4}_{\text{Epsom salt}} = \underbrace{BaSO_4}_{\text{Blanc fixe}} + \underbrace{MgCl_2}_{\text{Magnesium chloride.}}$$

In both cases, in addition to blanc fixe, the chloride corresponding to the sulphate used for precipitating is obtained, and these by-products must be eliminated from the blanc fixe by repeated washing. The precipitates of blanc fixe obtained by these methods differ considerably, a fact becoming distinctly noticeable even in the washing process. Whereas the white precipitate, produced by means of sulphuric acid, settles down to the bottom very quickly, and leaves the supernatant liquid perfectly water-clear, the precipitate obtained with the sulphates aforesaid subsides very slowly, and the supernatant liquid is always milky. The explanation of this difference between bodies apparently identical is found in the different structure of the precipitates. That obtained with sulphuric acid is more crystalline than that produced by the sulphates, which is more amorphous. Consequently the last mentioned method of precipitation furnishes a product with far more covering power than the other. This circumstance is very important, especially with regard to the application of blanc fixe for the manufacture of wall and fancy papers.

The decomposition of witherite with hydrochloric acid is always accompanied by very strong evolution of carbonic acid gas, the witherite being chiefly composed of barium carbonate ($BaCO_3$). The following equation explains the chemical process:

$$\underbrace{BaCO_3}_{\text{Witherite}} + \underbrace{2\,HCl}_{\text{Hydrochloric acid}} = \underbrace{BaCl_2}_{\text{Barium chloride}} + \underbrace{H_2CO_3}_{\text{Carbonic acid.}}$$

The combination H_2CO_3, however, is really not able to exist in the acid as such, and decomposes, at the moment of formation, into carbonic acid, CO_2, and water, H_2O, so that the above formula should really be expressed as follows:

$$\underbrace{BaCO_3}_{\text{Witherite}} + \underbrace{2\,HCl}_{\text{Hydrochloric acid}} = \underbrace{BaCl_2}_{\text{Barium chloride}} + \underbrace{H_2O}_{\text{Water}} + \underbrace{CO_2}_{\text{Carbon dioxide.}}$$

The important advantages gained by producing barium chloride from witherite are obvious and intelligible to every one. First, barium chloride is obtained direct from the raw material without the long and expensive calcining process necessary in the decomposition of barytes; and, secondly, the cost of removing the poisonous sulphuretted hydrogen is saved entirely. However, most brands of witherite sometimes contain a larger or smaller percentage of sulphur compounds, which furnish sulphuretted hydrogen when the mineral is decomposed with hydrochloric acid, though the quantities of this pernicious gas so formed are too small, in most cases, to cause any inconvenience to the vicinity.

The carbon dioxide formed in great quantities by dissolving witherite with hydrochloric acid may be allowed to escape into the open air, this compound (witherite) being generally harmless, though, of course, the gas must not be allowed to enter the workrooms. Certain kinds of witherite, however, contain considerable quantities of arsenic, the presence of which should be confirmed by chemical analysis beforehand, since when this substance is detected special precautions are necessary. In presence of hydrochloric acid these arsenic compounds form arseniuretted hydrogen, which is known to have an extremely poisonous action on the human organism.

Manufacture of Barium Sulphide from Barytes

The reduction of barytes to barium sulphide with coal is best effected in a retort furnace. The retorts, constructed of fireclay tiles, are built into a furnace one above another, and also side by side, in such a manner that they are uniformly heated. The openings for charging and emptying the retorts must be fitted with air-tight covers. The retorts themselves are provided in the upper part with one or two slits, to permit the unrestricted escape of the carbon monoxide and the products of combustion given off in large quantities.

Such enormous volumes of these gases are produced, especially when lignite is used as the reducing agent, that if two retorts are arranged one above the other the gases can be used as fuel. The gas, in this case escaping from the slits of the under retort, arrives at the bottom heating-place of the upper retort, comes in contact with the heating-current, and takes fire, a sufficient draught of air being present. Some idea of the quantity of gas can be gained from the fact that when the retort is opened—say for stirring the glowing mass—the sudden draught of air drives the flame out of the retort to a height of 7 to 10 ft.

The reduction of barytes in closed retorts is preferable to other methods for various reasons. First, this process has the advantage of preventing any reoxidation after reduction, which is not always the case when reduction is effected in reverberatory furnaces. If in this type of furnace the flame is compelled to pass through a medium-sized opening from the combustion chamber into the reducing-chamber, as is usual in modern furnaces of this class, the flame, even if it does not exactly oxidise, will at least hinder reduction. Properly speaking, the conditions for oxidation are high temperature and unrestricted admission of air. The delayed reduction in the reverberatory furnace is clearly indicated by the circumstance that oxygen is supplied by the flame itself to the easily oxidised body, carbon, mixed with the barytes, and usually causes it to ignite. This counteracts the object with which the carbon is added—namely, to deprive the barytes of oxygen, by utilising the same for its own combustion. A secondary consequence is that the reduction, eventually brought about by the action of the hydrocarbon gases of the flame, will require more time and carbon than should properly be necessary. Moreover, direct oxidation of the barium sulphide will inevitably happen in such reverberatory furnaces if the charge be allowed to remain too long; that is to say, after all the existing carbon of the mixture has been oxidised and has escaped as carbon monoxide. These defects will not occur if the mixture of barytes and carbon be calcined in closed retorts. The glowing retort ignites the carbon mingled with the barytes, and in the absence of a supply of air forces it to take from the barytes the oxygen necessary for its own combustion. The reduction is necessarily complete, provided sufficient carbon has been mixed with the barytes to convert the oxygen of the latter into carbon monoxide.

According to practical experience, this quantity amounts to rather more than a quarter—in fact, about three-eighths; that is, 37½ per cent.—of the weight of the barytes. Any lower quantity than this will result in a diminished yield of barium sulphide, whilst any excess of carbon will retard the dissolving of the calcined product, and is, moreover, uneconomical.

The tendency to reoxidation to which barium sulphide is prone, especially in the hot state, is prevented in the retorts, since the strong draught through the gas openings prevents the entrance of either air or flame. Besides, the construction of these openings is arranged in such a manner that the draught is restricted to the direction of the main draught, and cannot be reversed. Therefore it is immaterial, if the retorts be closed as directed, if the glowing mass be sometimes accidentally left longer in the furnace than is absolutely necessary.

A further advantage is the simple construction of the retorts. Charging and emptying are effected quickly and without difficulty, a point advantageous both to the working of the process and to the workman, the latter being exposed only for a short time to the heat and the poisonous carbon monoxide gas, as well as to the fine, corrosive dust of the barium sulphide, which makes respiration difficult.

In a retort furnace, even if only of medium size, twice the amount of material can be calcined with the same quantity of fuel as in a reverberatory furnace of far greater dimensions.

The process is continuous. Since the mixture of barytes and coal takes exactly four hours for complete reduction, one retort has to be filled every hour in starting, so that by the time the last retort is charged the first is ready for emptying. While this is being recharged and closed, the emptying of the second one can be commenced, and so on. In this manner the men are able to work continually without any prolonged waiting. After the glowing material has been in the retort two hours it should be turned once, an additional reason for this being that, on opening the retort, any internal pressure of gas perhaps is relieved. At the first thrust made into the glowing mass the gas ignites at once, and as soon as it is burned off and the smoke has escaped a little, the turning must be finished quickly and the retort shut again. The whole operation is so rapid that no oxidation need be feared. The mixture, as already mentioned, consists of one part barytes and three-eighths part coal (preferably lignite) that has first been crushed in an edge-runner mill and then ground by a set of stones as finely as possible.

It is advisable to run the mixture again through the stones after it has been mixed by the edge-runner. The resulting intimate mixture is then moistened in a suitable box of wood or iron plate, worked up well with a hoe or a shovel, then formed into bricks and well dried, either on the top of the furnace, or, if time allows, in the open air. At all events the bricks must be dry, if only for the reason that otherwise the residual water, would vaporise on calcination, and convert the barium sulphide into barium hydroxide, thereby retarding reduction.

With regard to the coal, a good deal depends, of course, on the quality, experience showing that bituminous coals are not so suitable for reducing as lean coals. Coals of the former class very often cause the mass to cake together, and consequently the reduction is very imperfect. With care the charge will yield an amount of barium sulphide corresponding to the original quantity of barytes; this maximum, however, cannot always be obtained, and in most cases about 10 per cent. of the barytes is left unchanged in the calcined product. On the other hand, careless mixing of the raw materials may result in 80 per cent. or less of the barytes remaining unchanged. The duration of the calcining process depends on the weight of the charge and especially on the degree of fineness of the powdered barytes employed, the more or less efficient mixing of the powdered barytes with the lignite having also a considerable influence on the time required for calcining.

No less important for obtaining favourable results is the purity of the barytes. The presence of iron is immaterial, but any large percentage or calcium carbonate or of calcium sulphate (gypsum) is a considerable disadvantage in respect of the yield obtained. It is therefore advisable to use the best barytes only.

If the reduction has advanced sufficiently far, which is indicated by the cessation of the blue flame of carbon monoxide, the glowing mass, which will already have crumbled down into a powder, can be drawn out of the retort quickly with an iron crutch. The finished product falls into an air-tight iron box below, and is there left to cool down to a faint red heat, at which point no oxidation of the barium sulphide need be feared. The box may then be opened and the cold powder packed in barrels for storage.

To convert barium chloride into the barium sulphide, it is next treated with hydrochloric acid until completely decomposed. This process can be carried on in ordinary wood tanks, as represented in Fig. 1. As already mentioned, the reaction is accompanied by the liberation of a considerable quantity of sulphuretted hydrogen gas, which has to be got rid of without making a nuisance. This can be done most simply if no other use be found for the gas, which will usually be the case, by carrying on the dissolving process in a spacious tank provided with a tightly closed cover. Near the edge of the latter is a short square wooden chimney, which is connected with a wooden pipe discharging into the chimney stack, thereby forming a passage through which the gas is discharged into the stack. The necessary draught for this purpose is admitted through an opening in the wall of the tank, the rate of discharge being controlled by a rotary damper covering the said opening. The tank is also provided with a mechanical stirring device, the vertical shaft of which passes down through the centre of the lid. Exactly opposite to the gas outlet the lid carries a hopper, situated near the edge and closed at the lower end by a horizontal slide. This hopper, which is closed by a well-fitting lid, delivers the powdered barium sulphide into the tank. Close to the interior jacket surface of the tank is placed a strong earthenware pipe extending nearly to the bottom of the tank and issuing from the side of the same about three-fourths of the way up. This pipe terminates at the upper end in a suitable fixed funnel, through which the hydrochloric acid is poured into the tank. The process begins by filling the hopper with barium sulphide, and then closing the lid. The weighed quantity of hydrochloric acid is then poured in through the earthenware funnel, and the stirring apparatus is set to work At the same time the slide of the charging-hopper is opened by degrees until the whole of the barium sulphide powder has run into the tank, whereupon the slide is shut and the hopper refilled with barium sulphide. This operation is repeated as long as there is any excess of hydrochloric acid in the tank, or, when working on a very large scale, until the tank is filled as far as practicable. In the latter case the quantity of barium chloride produced depends naturally on the size of the tank, and must be ascertained by experiment.

The acid may be added all at once or in small portions, as convenient, the method of working and the result being exactly the same in both cases. Since the barium chloride solution is to be precipitated with sulphuric acid later on, a little excess of hydrochloric acid will not matter, because, as already seen, the precipitation of the blanc fixe is accompanied by the production of hydrochloric acid, which, together with the excess, can be used for decomposing a fresh quantity of barium sulphide. If, however, the precipitation be effected with sulphates, any excess of hydrochloric acid is so much loss, because in this case the acid will be removed in washing out the blanc fixe and wasted. Hence, when precipitation with sulphates is contemplated it will be preferable to work in such a way that a small excess of barium sulphide remains in the tank. This can be decomposed in dissolving the next charge, unless allowed to run to waste.

The decomposition of barium sulphide with hydrochloric acid is not complete in the cold, and therefore, to obtain a perfectly neutral solution, it will be preferable to secure a more rapid liberation of sulphuretted hydrogen by blowing steam into the barium chloride solution towards the end of the operation. By heating the liquid, the final traces of sulphuretted hydrogen will be entirely expelled, its complete disappearance indicating that solution is complete even though a small excess of barium sulphide be present. The liquid must then be left to stand for some time, so that the impurities, chiefly natural mineral admixtures and decomposed barytes, surplus coal, and sulphur partly formed in the preceding operation, may gradually settle down. The clarified solution of barium chloride can then be drawn off and run into the tank provided for precipitating the permanent white.

It is not advisable to filter the *whole* liquid unless it can be put through a filtering press, since for many reasons this operation cannot be effected with the ordinary appliances at disposal more quickly than the impurities will settle down of themselves if left in a perfect state of rest. A better way is to filter the remainder of the liquid left in the tank after removing the cleared solution of barium chloride, and to mix the filtrate with a subsequent batch of pure solution.

In many works the next operation, the precipitation of the barium chloride solution with sulphuric acid or sulphates, is still effected in a manner that gives no data for exactly calculating the yield obtained. The precipitating agent is added at random, without being weighed and without considering the concentration of the solution or the acids. Apart from the fact that such a primitive method of working is not at all businesslike, it will never give a uniform product, and the resulting irregularity of structure, purity of shade, &c., will inevitably be the cause of many difficulties with the purchasers. This can be easily avoided by calculating the weight exactly. The Tables given in the Appendix show what weight of solid barium chloride will be formed in the tank, and what quantity of acid or sulphate will be needed for precipitating the same; and in this manner sufficiently exact data will be obtained to enable an exact calculation of the finished product to be made. This is the more necessary because the low price of blanc fixe leaves only a relatively small profit, and therefore even the smallest advantage must be seized.

For calculation purposes it is first of all necessary to know exactly how much space is occupied by the barium chloride solution. If the tank can be considered as a hollow cylinder, the volume can be ascertained from the mean internal diameter and the height of the column of liquid. On then determining the specific gravity of the barium chloride solution by the methods already mentioned, and finding from the Tables the weight of solid salts corresponding to the percentage value of the result, all the data needed for an accurate calculation will be obtained.

Having thus found the real weight of solid barium chloride present, it will be easy (by means of the molecular weight and the chemical equation expressing the process of precipitation) to calculate the quantity of sulphuric acid or sulphates needed for precipitation. When this has been gone into very carefully it will be found, on carrying it into practical performance, that theory and practice will be in very close agreement. In working on the large scale the precipitation process is performed as follows:

1. *Precipitation with Sulphuric Acid*

The precipitation tank, charged with the solution of barium chloride, is provided with wooden stirrers, which, in view of the large quantities of acid used, should not have any more metal fittings than absolutely necessary in the parts immersed in the liquid. The weighed quantity of sulphuric acid should be diluted to 20° B. in a second smaller tank, placed above the precipitating tank, so that the diluted acid can be run down into the latter. In dilution the sulphuric acid must be poured carefully into the cold water already in the tank (not *vice versâ*). When an intimate mixture of the acid with water has been obtained by thorough stirring, the stirring machine in the precipitation tank is set in motion, and the acid is run slowly into the barium chloride solution. The white precipitate (permanent white) is formed at once. When the whole of the weighed quantity of acid has been run in, a small sample must be drawn after some minutes, but without stopping the stirring machine. This sample is filtered through paper in a small glass funnel, and the filtrate is tested for any excess of barium chloride or pure sulphuric acid. For this purpose a drop of sulphuric acid is added (by means of a glass rod) to the filtrate, and if a white precipitate is formed the presence of a considerable quantity of free barium chloride is indicated. If only a faint cloudiness is observed the stock of barium chloride may be regarded as almost exhausted. If the addition of sulphuric acid produces no change in the filtrate it will be evident that either the precipitation has been effected exactly without any surplus of either barium chloride or sulphuric acid, or else that there is an excess of sulphuric acid. To make sure, a second sample must be taken from the precipitating tank (or the filtrate of the first sample should have been divided into two equal parts at the outset), filtered as above, and tested with one drop of a solution of barium chloride. If a strong white precipitate is formed, too much sulphuric acid has been used, but if there is only a faint turbidity, it will show that the proper quantity of acid has been only slightly exceeded. According as the above tests reveal a surplus of barium chloride or of sulphuric acid, the existing deficit must be corrected: in the former case by a fresh addition of sulphuric acid, and in the second case, by adding a corresponding quantity of barium chloride solution. The quantities to be added will depend on the amount of the precipitates obtained in the examination of the filtrate, and with a little practice can be gauged without difficulty.

After correction a new sample must be drawn to ascertain if all is in order. It will be evident that the supplementary additions of the one or the other ingredient must be weighed, and the quantities added to the total amount of barium chloride or sulphuric acid used.

Complete precipitation having thus been ensured, the precipitate is allowed to subside and the supernatant clear hydrochloric acid drawn off in a tank provided for this purpose, which done, the washing of the permanent white can be performed.* The washing waters must be renewed so long as free hydrochloric acid continues to be revealed by test-paper, *i.e.*, until not more than a faint red tinge is imparted to a strip of blue litmus paper dipped into the washings. When this neutral point is reached, the precipitate is filtered either in baskets, lined with filtering cloth (Fig. 11), and then squeezed to the required consistence in a press (Figs. 19 and 20), or else it is treated on a filtering press which does both these operations at once.

2. *Precipitation with Sodium or Magnesium Sulphate*

These precipitating reagents are used in the same manner as described above, except that it should be noted that hot precipitation greatly facilitates the subsequent washing of the precipitate, which, for reasons already mentioned, here requires a much longer time. In this process the operations begin with the preparation of the solution of sulphate, which can be effected in the tank used, in the preceding method, for diluting the sulphuric acid. For this purpose, if hot precipitation is in question, the tank must, of course, be provided with a steam pipe. The weighed quantity of sulphate is placed in the tank, which is then filled about three parts full of water, steam being admitted, and the mixture kept stirred until all has been dissolved, whereupon the temperature is raised to 70° or 80° C. Commercial sodium sulphate being always more or less contaminated with impurities which separate on dissolving the salt, these solutions must be left a certain time before using, until the impurities have settled down. The same applies to the use of magnesium sulphate (Epsom salts). The succeeding operations are exactly the same as in the method of precipitation with sulphuric acid, and therefore need not be repeated. As already mentioned in the beginning of this chapter, the resulting by-products (sodium chloride or magnesium chloride) are almost worthless, and have no injurious effect on the resulting blanc fixe, so that no such careful washing as is necessary with the sulphuric acid process is required here. However, if an absolutely pure product be desired, the chlorides in question may be tested for by adding a drop of silver nitrate to a small sample that has been drawn from the washing water and acidified with nitric acid. In the absence of the chlorides no turbidity will be apparent in the liquid.

To obtain the whitest possible product very pure water is required, especially for dissolving the barium chloride. Experience shows that water containing dissolved organic matter or iron has more or less influence on the purity of shade of blanc fixe. The presence of compounds of calcium or magnesium in the water is of little or no importance, and any disturbing effect such impurities might have can be prevented by slightly acidifying the barium chloride solution before precipitation.

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* It is evident that only the first runnings of hydrochloric acid can be used for dissolving fresh quantities of barium sulphide, the subsequent washings being useless.

Manufacture of Permanent White from Witherite ($BaCO_3$)

From a technical standpoint there is little difference between this process and that of making artificial barium sulphate from barytes, apart from the reduction of the latter into barium sulphide, the apparatus and manipulations being the same in both cases. There is, however, a difference, inasmuch as the carbon dioxide gas liberated by the raw material witherite on dissolving the latter in hydrochloric acid is a less inconvenient product, so that the process of manufacture is greatly facilitated. On the other hand, the dangers of an atmosphere highly charged with carbon dioxide must not be under-estimated. As soon as the barium chloride has been formed operations already described for the production of permanent white are performed, and furnish the same product as in the former method.

The gas liberated on dissolving witherite in hydrochloric acid is the inodorous carbon dioxide instead of the sulphuretted hydrogen given off from barium sulphide. This circumstance offers the advantage of enabling the dissolving process to be carried on in any well-ventilated work-room, which cannot be done when barium sulphide is being treated, since in spite of all precautions the sulphuretted hydrogen cannot be prevented from escaping through the cover of the tank into the atmosphere of the room. In such event this gas is a source of injury not only to other colours in course of manufacture there, but also to the workmen engaged. Exhausts, however, will be very useful in this respect. To facilitate solution it is advisable to use the witherite in a very finely divided state. The operation itself can be effected in exactly the same way as with barium sulphide, and therefore need not be described in detail. It must, however, be mentioned that the process of solution will be greatly facilitated by admitting steam from the outset. The muddy residue left in the tank after the saturated solution of barium chloride has clarified is often very large, but in all cases is absolutely worthless and is thrown away.

If a very pure witherite is used and a chemically pure blanc fixe is not essential, the witherite can be treated direct with diluted sulphuric acid. The impurities deposited in such case with the precipitated colour can be sufficiently removed by a simple process of levigation.

Experience shows that the operation is facilitated by adding a small quantity of hydrochloric acid to the sulphuric acid. This effect can be explained on mechanical grounds, inasmuch as the hydrochloric acid dissolves part of the witherite, the soluble product being at once converted into sulphate by the sulphuric acid, which liberates the hydrochloric acid again and enables it to react progressively on fresh portions of the witherite.

Until recently blanc fixe was mostly put on the market in the form of a stiff paste containing 15 to 20 per cent. of water. It is therefore important to maintain a certain standard of moisture content, and to test each batch for this purpose while it is still in the press. This test is applied in the following simple manner: A sample of 50 grms. is taken from the paste in the press at intervals and dried. When the sample is perfectly dry the temperature employed is immaterial; it is weighed again, and the loss in weight multiplied by 2 gives the percentage of water in the paste. For instance:

Weight in paste form 50 grms.
„ when dry 42 „

Loss . . 8 × 2 = 16 per cent. water.

It is in this state of wet paste that blanc fixe finds its most extensive application in the manufacture of wall and fancy papers. It is less used for the purpose of painting in oil, and is rarely so employed in a pure state, although it would seem to be very suitable for this purpose on account of its absolute permanence, a quality in which many other colours are lacking. Blanc fixe, however, is deficient in covering power, though the artificial product is superior in this respect to natural barytes, be the latter ground never so fine or so often. According to Meissner, a blanc fixe suitable for oil paints may be obtained by taking the product formed by precipitation with sulphates (*not* sulphuric acid), calcining it very strongly when dry, then quenching it in cold water, re-drying, and grinding it to a fine powder.

So far as oil painting is concerned, blanc fixe is used as an adjunct, either for mixing with white lead, zinc white, making cheap brands of Prussian blue and for similar purposes, or as a white base for light shades, for which purpose it is especially suitable on account of its pure whiteness and permanence.

As a rule blanc fixe made from witherite is of a purer white than that obtained from barium sulphide.

The quality of blanc fixe may be tested by mixing it to a workable consistency with a 2 per cent. solution of glue, and applying it on strips of paper. When dry, these coatings must be pure white, and adhere firmly when crumpled under moderate pressure. Failure to stand this test indicates insufficient grinding or imperfect washing (removal of acid).

Blanc fixe is easily detected by analysis, owing to its power of resisting the usual reagents. Boiling concentrated sulphuric acid has a slight solvent action, but barium sulphate is re-precipitated from solution on dilution with water. In mixed colours and as an adjunct, blanc fixe can be detected by chemical means in the incineration residue insoluble in acids.

Attempts have also been made to make a white pigment from another alkaline earth allied to barium, namely, strontium. The raw material in this case is the native strontium sulphate, cœlestine, which is treated in the same way as barytes. This strontium white is said to be permanent, and also to be superior to blanc fixe in covering power, besides being specifically lighter. It has not, however, found any general application.

II.—MANUFACTURE OF ZINC WHITE

(*Flowers of Zinc, Snow White, Blanc de Zinc* (*de Neige*), *Fleurs de Zinc, Zinkweiss*)

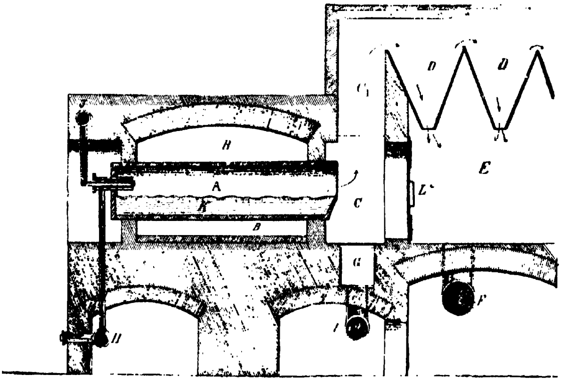
Zinc white is zinc oxide, a compound of metallic zinc with oxygen, having the chemical formula ZnO. It is prepared in large quantities from the metal itself, as well as directly from ores. The manufacturing process is based on a remarkable property of zinc, namely, that when heated to a temperature higher than its melting-point it disengages vapours that burn in presence of air—*i.e.*, undergo oxidation. The product of this combustion is zinc oxide, the above-mentioned zinc white of commerce. The zinc oxide being non-volatile, settles down on the cooler parts of the apparatus in the shape of downy white flakes. This interesting process can be easily observed by the following experiment. Finely granulated metallic zinc is mixed with charcoal, and the mixture heated in a crucible of graphite or fire-clay. At a temperature only slightly exceeding the melting-point of the metal, faint white fumes are produced, increasing as the temperature rises. Finally, owing to the free access of air, the zinc burns with a bright greyish-white flame, indicating the actual process of oxidation resulting in the aforesaid white vapours (zinc fumes), which on condensation form the zinc white of commerce. To make this condensation, and consequently the yield of zinc oxide, as complete as possible, the white vapours are collected in special chambers, where they cool quickly and settle down as delicate white flakes. On a small scale this experiment will succeed best when the crucible is covered with a conical top of sheet-metal in such a way that sufficient air is admitted freely to the glowing mass in the crucible. On connecting the narrow opening at the apex of the cone with another vessel—a sheet-metal case, for instance—provided with a small opening to produce a suitable draught, nearly all the resulting zinc white can be collected.

The manufacture of zinc white is conducted on exactly the same principle, except that in this case cylindrical retorts are used instead of the crucible to melt the zinc. Moreover, the formation of the zinc oxide proceeds in different stages, the first being the conversion of the metal into volatile fumes. The second stage consists in the burning of these fumes by a superheated current of air which meets the zinc fumes at the proper moment. The third and last stage is the condensation of the resulting zinc oxide in separate chambers maintained at a temperature facilitating the deposition of the zinc white. The oxidation in the first and second stages of the process is accelerated by the simultaneous admission of carbon monoxide or carbon dioxide and atmospheric air into the retorts. A further reason for the admission of air from the outside is to ensure the complete combustion of the impurities which are generally present in carbon monoxide gas (soot, ashes, &c.), and might pass into the zinc white and lessen the purity of the colour.

The retorts used for melting and vaporising the metallic zinc are long cast-iron or clay cylinders of oval cross-section, closed in front but half-open at the rear end. According to the size of the works, 10 to 20 of these retorts are built into a reverberatory furnace usually in two rows, one above the other, in such a manner that the rear ends of all the retorts discharge into a transverse flue. Sometimes two sets of retorts, mounted back to back, are arranged in the one furnace. In this flue the zinc vapours issuing from the retorts meet a current of air heated to 300° C., which converts them into zinc oxide, the latter being then conducted into the condensation chambers. The supply of carbon monoxide gas to the retorts is furnished by a coke oven placed outside the furnace and connected with it by a circular brick flue from which iron or earthenware branch pipes conduct the gas through the doors of the retorts to the interior. The pipes for the supply of air are connected with a main flue communicating with the outside air, and are preferably mounted inside the wider gas pipes, so that in both pipes the draught follows the same direction—*i.e.*, in line with the longitudinal axis of the retort. The air-current for oxidising the zinc vapours can be heated in the furnace used for heating the retorts.

In beginning work the retorts are charged with crude zinc, closed, and then raised to white heat. Meanwhile the gas and cold air supply-pipes are put into position, and the joints luted with fire-clay paste. The formation of zinc oxide being in full swing, the separated flakes of zinc white are driven out of the hot-air flue by the strong draught and reach a series of brick chambers. Here they settle down in tapering iron hoppers, and gradually fall, under the accumulated weight of the mass, into bags hung at the mouth of the hoppers, which bags are emptied from time to time.

FIG. 56.



A, retort.
B, furnace.
C, main flue for all retorts, or for the supply of hot air.
C_1, flue leading the vapours of zinc into the cooling-chamber *E*.
D, *D*, collecting hoppers.
E, cooling or condensing chamber.
F, *F*, *G*, ventilators for cooling with cold air.
H, air main leading from the outside into the retort *A*.
J, carbon monoxide flue leading into the retort *A*.
K, molten zinc.
L, door between *C* and *E*.

The manufacture of zinc white directly from the ores is carried on in a very similar way, so far as the oxidation of the zinc vapours and the subsequent condensation are concerned. The roasted ores are spread on the hearth of a furnace heated with coke or anthracite, and are thus raised to a white heat. By means of a system of pipes a current of air is admitted below the hearth, and is distributed uniformly to all sides so as to convey the escaping vapours to the oxidising flue, where they are exposed to a very high temperature and are completely converted into zinc oxide. The latter is then deposited in the adjoining precipitation chambers. The zinc oxide deposited nearest the retort contains particles of metallic zinc that, settling down a little farther off, is coarse and heavy, whilst the delicate flaked zinc oxide is deposited in the rear end of the precipitation chambers. In this way a kind of fractional separation of the product, according to quality, is obtained. The lightest product is the most valuable. The manufacture of zinc oxide is not carried on largely in colour works, being chiefly confined to works engaged in the metallurgical treatment of zinc.

The purity of the various commercial brands of zinc white chiefly depends upon the purity of the metallic zinc used, and to a smaller extent on the more or less accurate working of the producing apparatus and on the care bestowed on the process. Thus it may happen as a result of careless management that the impurities introduced in the retorts by the carbon monoxide gas are imperfectly consumed, or that the supply of hot air is deficient. In the first case, dust and soot get into the precipitating chambers, whilst the second circumstance entails an imperfect oxidation of the zinc vapours. In either event an inferior grey product results.

The zinc grey of commerce is a zinc white containing a portion of unoxidised metallic zinc. This product is also used for oil paints.

Zinc white of a brownish shade, prepared from zinc ores containing cadmium, may often contain cadmium, but as the latter is more valuable, it is to the interest of the manufacturer to recover it. This also applies to zinc oxide containing antimony.

Zinc white is obtained as a by-product in the recovery of silver from silver-lead by the Cordurié process. This process consists in obtaining an alloy of silver and zinc, and then passing steam over the hot mass. This steam leaves the silver in the metallic state, whilst zinc oxide is formed and is carried off by the current of steam to be condensed in suitable chambers.

According to Germain, roasted zinc ores can be treated by the wet process with a hot solution of ammonium chloride, which attacks the metals but zinc oxide only. On cooling, a double salt of zinc and ammonium is deposited from the filtered solution, which salt decomposed in boiling water throws down zinc oxide as a dense precipitate.

Zinc white obtained by calcining zinc carbonate has a yellow shade, and is inferior to that produced by direct oxidation. Zinc white is non-poisonous, and is very fast to air and light. Moreover, it is unaffected by corrosive and sulphureous gases, and is therefore specially suitable for mixing with other colours, since it does not alter their tone. Zinc white can be used as a water or oil colour, but the latter dries very slowly. The covering power is considerable, but not so good as white lead.* Pure zinc white should not contain more than two per cent. of moisture. It should dissolve in diluted hydrochloric acid to a clear solution without any residue—any effervescence indicating zinc carbonate or some other carbonate. A residue insoluble in acid shows adulteration with barytes, china clay, &c., and should be analysed. The acid solution, when supersaturated with ammonia and treated with ammonium sulphide, gives a white precipitate of zinc sulphide. A dirty white precipitate indicates the presence of other metals. The filtrate should not leave any residue when evaporated and incinerated on platinum foil.

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* According to Wagner, however, 10 parts of zinc white should cover the same surface as 13 parts of white lead.

Bengal

III.—MANUFACTURE OF WHITE LEAD

(*Bleiweiss, Céruse, Blanc de Plomb, Flake White, Krems White*)

White lead is one of the most important artificial pigments made, and its technical application, especially for painting in varnish, is far more extensive than is the case with any other mineral colour.

Although the use of this pigment has been restricted considerably in some countries by stringent legislative enactments regulating the use of white lead on account of its injurious properties, and endeavours have been made to find equivalent harmless substitutes, the manufacture of white lead is still pursued on a very large scale. Of the innumerable substitutes proposed for white lead, only zinc white and the lithopones (to be described later on) are used to any extent. In many cases, however, these compounds are incapable of fully replacing the valuable properties of white lead.

According to its chemical composition, white lead is basic lead carbonate $2\ PbCO_3 \cdot Pb(OH)_2$, and therefore must not be confused with the neutral lead carbonate, $PbCO_3$. The excellent properties of white lead are probably due to its content of lead hydroxide, $Pb(OH)_2$, since experience shows that these properties increase with the percentage of the hydroxide, but diminish when the proportion of neutral lead carbonate is increased.

The artificial manufacture of white lead probably dates from very remote times, and various circumstances point to Holland as the earliest seat of the industry. It may be assumed with certainty that in the course of time the manufacture of white lead spread from Holland all over Europe, the various processes now in use having probably been elaborated through the introduction of more or less successful improvements and appliances. No very keen perception is needed to see in the later methods of manufacturing white lead an endeavour to shorten as much as possible the protracted reaction inherent in the Dutch process, and at the same time to obtain a whiter product. This problem seems to have been solved most successfully by the subsequently introduced German chamber process, for, whilst the Dutch method gradually became less popular, the German method of production continued to make headway in Central Europe, and especially in Russia, so that to-day by far the greatest quantity of white lead is made by this process. In fact, the primitive Dutch process by no means corresponds to modern views in the colour industry, and therefore in the following pages the description of this method will be summarised briefly, as being rather out of date.

In France, and in some parts of Germany as well, the French process of making white lead was introduced, and at first seemed to surpass the German method in point of speed and the great purity of the product. It was, however, soon discarded, the resulting white lead being of inferior covering power, and yielding paints of low stability. From this it may be assumed that the French process does not yield a proper white lead, but only a product which, chemically speaking, more closely approximates to neutral lead carbonate than to basic lead carbonate. The behaviour of the former carbonate under the influence of light and air is at least very similar to that of French white lead, and lends favour to the above hypothesis.

The English method (erroneously termed the American method), though claimed to be simple and to yield a product of high covering power, has not succeeded in gaining popularity, and is therefore presumably defective.

a. The Dutch Process

The chief factor in this process is the form in which the metallic lead is used, inasmuch as a very large surface is desirable to facilitate the action of the substances decomposing the metallic lead—viz., acetic acid and carbonic acid, as well as the oxygen of the air. The most suitable form for both the Dutch and German processes is that of thin strips made by pouring the molten metal into suitable moulds.

In the Dutch process these metallic strips are rolled up spirally, and placed in earthenware pots (glazed inside) in such a manner as to avoid direct contact of the lead with the vinegar in the bottom of the pot during the whole corroding process. The pots are then covered with lead plates, and a large number are buried together in horizontal and vertical rows in horse-dung, tan bark, or similar fermenting materials. The process of fermentation through which these materials gradually pass provides sufficient heat to evaporate the vinegar in the pots. In this vaporised state, assisted by the action of atmospheric oxygen, the vinegar converts the metallic lead into basic lead acetate $Pb(C_2H_3O_2)_2$, $2Pb(OH)_2$, which latter in turn is decomposed by the carbonic acid (carbon dioxide) produced at the same time into lead carbonate and neutral lead acetate. This process generally takes several months to complete.

The first stage in the Dutch process is to obtain the lead in a suitable form for use; and as this operation is also of prime importance in the German white lead process, it will now be dealt with thoroughly.

The most convenient method of melting lead is in strong cast-iron pans mounted on projecting flat lugs in a furnace in such a manner that the flames can spread freely over at least three-quarters of the total heating surface of the pans. Lead being a very heavy metal, the pans, which should measure only 32 to 36 inches across, must have an extremely strong support, preferably by resting the bottom of the pan on three or four brick projections arranged in the hearth of the furnace. The pans are built into the furnace in such a way that the top surface of the furnace is flush with the upper edge of the pan. To protect the brickwork the surface round the pan is covered with strong iron plates to lessen the shocks produced by the heavy pigs of lead, and liable to loosen the structure.

When lead is melted for the first time in a new pan the operation proceeds very slowly, and generally requires a temperature far exceeding the melting-point of the lead. The reason of this peculiarity can be easily explained. Lead is sold on the market in the shape of oblong pigs rounded off on the top, as being the most convenient form for loading; and when a new melting-pan is being filled for the first time with such pigs the points of contact with the pan are of small area, so that the transmission of heat is retarded, this being aggravated by the open spaces between the pigs themselves. Hence the lead melts in small quantities only at the start. So soon, however, as the first pig is melted and the bottom of the pan is covered with molten metal, the second and following pigs will melt much more rapidly, since they dip very deeply into the liquid metal, and therefore the heat is transmitted more freely. This simple fact can be utilised in subsequent meltings. In casting the lead into strips the pan should never be completely emptied; at least enough lead should be retained to slightly cover the bottom of the pan.

As soon as a sufficient quantity of lead is melted, the lead strips are cast. This work should be done as quickly as possible, and therefore at least two workmen are required for the operation, one to pour the metal, and a second one to hand him the moulds and to remove the finished, *i.e.*, cooled, strips. The pourer must possess a certain skill and be experienced in the work, it being absolutely necessary for the regular course of the manufacturing process that the strips should be of exactly equal thickness. Since thin metal strips will corrode much quicker than thicker ones, it will be found on emptying the pots that whilst in those containing the thinner lead strips the formation of white lead is complete, those filled with thicker strips still contain more or less of undecomposed metal, which will then have to be remelted. In emptying the pots (or chambers) a certain unavoidable quantity of undecomposed lead is always found in the finished white lead, and the only possible way to diminish this obvious defect of the process lies in the skill and care bestowed on the moulding so as to produce strips of uniform thickness. Given a certain amount of practice, an intelligent workman will find no difficulty in carrying out this operation successfully.

The moulds used for casting are made either of strong sheet-iron or of cast-iron, the former being decidedly preferred, as, whilst fully answering the purpose, they are lighter and therefore handier. True, they get hot quicker than the cast-iron ones, but conversely will cool again sooner than the others.

It is a good plan to lay several—three to five—moulds on a common base plate, so as to produce a shallow frame divided by parallel partitions into a number of compartments each 4 to 6 inches wide. Five or six of these moulds are placed on a suitable wooden or iron rack close to the founder, so as to slope gently downward and from the founder towards the assistant who has to look after the emptying and changing of the moulds. The length of the moulds varies considerably in different works; some have a length of 20 to 36 inches and more. The shorter sizes are, of course, more convenient for handling, since they not only furnish strips of more uniform thickness, but also lighten the task of the workman. In the Dutch process the length of the metal strips depends on the size of the pots used, because unless the pots are properly filled the output is needlessly reduced.

When the corroding pots are to be covered with leaden lids, these also must be cast at the works. The size depends on the diameter of the pots. The moulds for casting must be arranged in such a way that the lead plates are recessed or stepped on the under side, so that the smaller part fits accurately into the neck of the pot, whilst the broader top portion of the lid will slightly overlap the mouth of the pot.

The metallic lead used by white lead makers contains a quantity of technical impurities, which will rise to the surface of the liquid mass in the melting. Special precautions must therefore be taken to prevent these by-products from entering into the metal strips and thence into the finished pigment. This can be prevented in a very simple way by pushing the floating impurities outward from the centre by the aid of a long-handled iron ladle, and then placing an iron ring about 12 to 14 inches in diameter and 2 to 3 inches wide in the clear space thus obtained. This ring floats on the surface of the lead by reason of its own lower specific gravity, and the founder can without difficulty ladle the perfectly pure molten lead from the interior of the ring. A slight oxidation of the lead will not affect the quality of the resulting pigment, though the contrary is often asserted. Lead oxide is corroded by acetic acid much more easily than the metal itself, and it is therefore immaterial if any parts of the oxidised coating get into the lead strips in the casting process, or if the castings film over with such a coating (blue tarnish) in gradually cooling. In fact, in these circumstances a more intensive reaction in the pots may be anticipated. On this account, and not with prejudice, endeavours are made in many works to obtain this blue tarnish in casting the strips.

It is impossible to give any further instructions for obtaining uniform lead strips by casting, so much depending on the local conditions, and at all events on the skill of the workmen. The founder takes an iron ladle, varying in size according to the quantity of metal to be cast at a time, and scoops out of the kettle a quantity of molten lead, which he pours into all the moulds, the second workman meanwhile lifting and lowering the moulds to make the metal flow evenly. All moulds having been filled in this manner, and the metal completely cooled, the moulds are replaced by another set and the operation is repeated. The moulds are emptied by simply turning them over, the lead plates then falling down on the surface underneath. Since the moulds soon get very hot, it is advisable to keep a large number at hand, so that they can be changed and the work carried on without any delay. They should not, however, be changed unless they have become so hot as to be difficult to handle or delay the setting of the metal, and thus retard the work, because generally it is an advantage to use moulds heated up to a certain degree, the heat assisting the metal to flow uniformly in all directions.

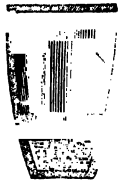
The pots used in the Dutch process are generally of the same shape as those used in olden times, though some manufacturers now employ those of stoneware instead of ordinary clay. This is a great improvement—even though the only one made in the process. Clay pots being thinly and badly glazed, offer but little resistance to the destructive action of the acetic acid, and very soon become useless, the acid trickling through the pores where the glaze has been removed. This defect, which in time will stop the reaction entirely, is precluded by the use of stoneware pots. The pot lids may also be advantageously made of the same material (stoneware), and preferably domed, since with this shape the horse-dung covering the pots can be easily removed after the process is ended, without any risk of dirt or straw getting into the finished pigment. Moreover, this risk is precluded by the fact that in most cases the lids are made to slightly overlap the edges of the pot.

The outside shape of the pots will be understood without any further explanations from Fig. 57.

Inside, at a certain height, which of course must be the same in all the pots, are three to four short projecting ledges on the walls, which support the spirally rolled strips.

The only materials used to generate, by their own fermentative decomposition, the heat and carbon dioxide necessary for the reaction, are horse-dung and common tan bark, whichever can be obtained cheaply and in the requisite quantity. In the choice of these materials no improvement has taken place in the Dutch white lead process for ages, unless the use of the different kinds of tan bark, amongst which willow tan bark is the best, can be considered as such, and even this change is confined to works favourably situated for obtaining these materials cheaply and in sufficient quantity. Ordinary tan bark can best be obtained from tanneries, and it is only spent tan that is suitable for the purpose of the white lead maker.

FIG. 57.



Before describing the method of burying the corroding-pots (sometimes erroneously termed calcination pots), it will be advisable to explain the fundamental principles of putrefaction.

In the chemical sense, putrefaction is the gradual atmospheric oxidation of the constituents of animal or vegetable organic substances. The final products are therefore always compounds of oxygen, such as carbonic acid (carbon dioxide), water, &c., and if the substances contained nitrogen there will also be formed ammonia, nitric acid, or their inferior stages of oxidation.

Every oxidation being a kind of combustion, the putrefaction of the materials used in the manufacture of white lead by the Dutch process must also be considered as such. Certainly there is no appearance of fire, as may be noticed in cases of violent oxidation, since the progress of this combustion is very slow, nevertheless the evolution of heat attending every process of oxidation may, in favourable circumstances, be in this case very considerable. Combustion, as is known, entails a diminution of the originally solid substance, the escaping oxidation products being mostly gaseous, and the substance should therefore be proportionally renewed when the process is desired to be continuous. These conditions operate in the preparation of white lead by the putrefaction of horse-dung or tan bark.

It is highly important that no interruption of the process of putrefaction and of the generation of heat should be allowed to occur as the result of external influences. Such interruptions may be caused primarily by an unfavourable external temperature, and the process of fermentation must therefore be carried on in closed rooms, which can be heated in winter time if the temperature falls too low.

Furthermore, the process may be retarded when the substances to be fermented are deficient in the moisture necessary for starting the process of fermentation. This condition is generally the result of the horse-dung or tan bark having accidentally got too dry before use; and, though renewed moistening of the materials will restart the fermentation after some delay, it generally soon subsides without having generated sufficient heat and carbonic acid to ensure the proper formation of basic lead carbonate.

The appliances for storing the reaction pots during the process of fermentation are called stacks. They are the same everywhere, being in fact so simple as to admit of but slight alteration; and any variations that may actually exist in different countries have been designed to overcome difficulties caused by the prevailing conditions of temperature. On the other hand, the dimensions and other features of the stacks depend on the space at disposal and the extent of the works. Therefore, in view of all these circumstances, it is very difficult to express the most advantageous dimensions for these stacks in definite figures. All that can be said is that for convenience in the subsequent dismounting of the stacks they should not be made so high as to put too heavy a strain on the lower row of pots, the weight of the material being very heavy in all cases. Given a suitable treatment of the materials, the height or width of the stacks will not affect the course of fermentation.

In making white lead in stacks, the first point to be taken into consideration in large works is to secure continuity in the filling and emptying of the stacks in regular order. At least six to eight stacks are required in order that each can be emptied and re-charged within a week. In very large manufactories this minimum can be correspondingly increased.

In a well-established white lead works the various compartments forming the separate stacks should be carefully boarded off, each being provided with a door opening outward. The number of the stack, the date of charging, and quantity of the charge should be inscribed on a tablet outside.

The work begins with spreading on the bottom a level coating of the material used for fermentation, which is then stamped down and thoroughly wetted by watering with an ordinary water-can. Upon this coating, which should not be too thick in tightly closed rooms, the stack is erected, the method pursued, however, differing according as the pots are to be open or lidded. In the former case special measures have to be taken to afford proper support to the roof sheltering the pots. This is done as follows. Another layer of the fermenting material is placed along the wall, up to about the height of the reaction pots, the latter being placed one beside the other in one row, parallel to the wall, pressing each pot tightly against the wall. Next, a 1½-inch board, somewhat broader than the height of the pots, must be set on edge alongside the pots and pressed fairly tight against them. The empty spaces thus left between boards and pots must be filled with dung or tan bark. When one row is finished and the pots are packed round with the fermentation material, the necessary quantity of vinegar must be poured in, and the coiled lead strips fixed, taking care that the latter do not come into direct contact with the acid. In the same way a second and third row, &c., must be laid side by side, with boards between the rows, until the whole of the available space is filled.

The whole surface of the first row of pots must now be covered with ½-inch boards laid crosswise over, and supported by, the former series. To prevent any impurities getting into the pots through the joints of the covering boards, each joint is covered by a third board, and in this way a very tight and perfect covering is obtained, resembling, for instance, the construction of wooden roofs.

The covering of the first layer is used to support the second, and so on, the operation being performed exactly as described until either the whole space is filled or a given number of pots have been stacked.

The arrangement of lidded pots is somewhat more difficult. In the case of open pots, the board covering of each horizontal stratum of pots can be walked on in setting the next layer, and so on without any further precaution. Now this cannot be done when the pots are fitted with earthenware lids without risk of displacing or breaking the lids, and thus disturbing the manufacturing process. In this case as soon as three to four rows have been laid they must be covered with a layer of dung or tan, and other horizontal layers put in position over them until the stack has been built up to its full height. When five to six rows have been put up in this way, a beginning is made on the opposite side of the chamber, setting up the same number of rows to the same height. The intermediate space—*i.e.*, facing the door—is afterwards filled with pots in the same manner, one above the other, working backwards until the door is reached.

In method of stacking care must also be taken that the hollow spaces left between the pots are thoroughly filled with tan or dung.

Whether pots are open or lidded, it is always highly important to cover the top layer with an extra thick stratum of the fermentative material, since this forms the safest protection against any adverse influence of the external temperature.

The extent to which leakages, due to accident or carelessness in packing the stack with fermentative material, can influence the process of fermentation is exemplified by the fact that the disengagement of heat is far greater in stacks where lidded pots are used than in those where the pots have been covered with boards. This difference is due to the hollow spaces invariably left between the boards and pots, especially near the top of the stacks, which spaces will be sufficient to retard the process of fermentation or cause it to stop altogether. Hence it may be concluded that pots provided with lids are more suitable than open pots for making white lead by the Dutch process.

The stacks having been built and examined to see that they are free from defects, they may be left alone to complete the work of corroding the lead. The commencement of the fermentation process will become manifest in the course of a few days. In proportion as putrefaction progresses, the temperature inside the stacks will rise, and an escape of steam will be noticed in places, increasing day by day, and affording an approximate indication of the progress of the reaction itself. As this escape of steam diminishes, the temperature in the stack sinks, until finally the disappearance of the steam shows that the cooling stage has been reached, whereupon it may be assumed that no more white lead will be formed. As there is no need to wait until the dung or tan cooled down further, the stack can be demolished at once. On taking away the fermentation material, none of it must be allowed to get into the pot. The dung or tan is mixed thoroughly with fresh quantities of the same materials, so that they can be used over again, whilst still warm, in building up new stacks.

If the fermentation materials have become quite cold and very dry, they must be mixed with fresh quantities, piled on heaps in suitable places, and the whole moistened by repeated sprinkling with water and turning. Under this treatment they will get warm again in the course of a short time, and then only will they be fit for use.

Instead of tan, dung, and similar substances, C. H. Vickermann, of Philadelphia, uses ordinary sumach, the torn dry fibres of stalks and leaves of which plant are said to be specially suited for the Dutch process, owing to the larger amount of carbonic acid liberated by this material than from tan, dung, &c., while no putrefaction products (sulphuretted hydrogen, &c.) capable of injuring the colour of the white lead are formed.

The pots should be emptied in separate rooms, to prevent contamination by the dirt in the stack. For this purpose the pots are cleansed of adhering dirt, and placed eighteen and twenty at a time in a box fitted with handles, and carried by two men into the emptying room.

On opening the pots it will be found that the coiled lead strips and the circular lead plates used for covering the strips (if such plates have been used) are covered with a more or less thick deposit of white lead, whilst the vinegar put into the pots at the start has nearly or quite disappeared. If the process has been conducted properly, only a very small quantity of unchanged metallic lead will be left in the pots. If, however, the process has been an imperfect one, it is quite possible that considerable quantities of the metal will be found unchanged. The same applies to the decrease of the vinegar by evaporation, which keeps pace with the reaction.

Whatever the result of the chemical process, the lead coils must be taken out of the pots very carefully, to avoid the crumbling of the extremely hard and tenacious coating of white lead, no correction being possible in the Dutch process. The lead coils are placed in large rectangular wood boxes, whilst any other residual contents of the pots are poured into tanks provided specially for the purpose.

The next operation, the separation of the white lead from the unchanged residue of metallic lead, and the further treatment of the former to obtain a marketable product, is exactly the same as with the German process, and will be thoroughly discussed in the following section.

b. The German Process (Chamber System of Corroding)

This process—known also as the "chamber process"—can be regarded, in the main, as the perfected improvement of a method carried on more particularly at Klagenfurt, Wolfsberg, Villach, and other places in Austria, to obtain a white lead of an extremely pure white shade. To acquire a proper idea of the development of this process, it will first be necessary to thoroughly examine the details of the operation as practised at Klagenfurt.

The Klagenfurt Chamber Process itself may in turn be regarded as a partly improved Dutch process. In both cases the formation of white lead takes place by the gradual influence of acetic and carbonic acids upon metallic lead under similar conditions. However, whilst in the Dutch process the heat necessary to form the white lead is, as already seen, generated by the natural fermentation of organic substances, in the Klagenfurt process the evaporation of the vinegar is effected by artificial heat. The carbonic acid is also produced by fermentation, this constituting a point of difference between the Klagenfurt process and the German chamber process, since in the latter the carbonic acid is artificially prepared. Now, in the former method no exact regulation of the process is practicable, owing to the special arrangement of the workrooms and the nature of the materials selected for producing the carbonic acid, whereas the chamber process affords the important advantage of control all the way through.

In the Klagenfurt process the vinegar is sometimes applied in the same way as in the Dutch process, that is, by pouring ready-made vinegar direct into the apparatus provided for this purpose and already charged with the metallic lead. In other cases the vinegar is made on the premises by fermenting grape husks, low-grade fruit must, or bad raisins. This method furnishes both acetic acid, which is at once vaporised by the artificial heat, and large volumes of carbonic acid, necessary for the formation of white lead. Both more or less completely effect the gradual corrosion (exactly as in the Dutch process) of the strips of metallic lead, the process taking four to six months, according to the capacity of the installation. For this purpose the metal strips are suspended on wooden rods so as to be duly exposed on all sides to the influence of vinegar fumes and carbonic acid.

It follows from this circumstance that the Klagenfurt white lead process must be carried on in closed rooms kept warm by special heating appliances on the outside. These rooms, which are also called stacks, are still generally arranged on the original lines, and only the German chamber process, based on the same principle, has made any advance and developed in accordance with modern views. Hence it will be sufficient to confine ourselves to the description of a single stack as arranged and used in the Klagenfurt process of manufacturing white lead.

The stacks are arranged in pairs, separated by a wide gangway and provided with special entrance doors. They are erected in strongly-built structures thirty to thirty-three yards long, which are divided into two storeys by a layer of strong beams arranged about half way up. The upper floor serves for the erection of the stacks, the lower one being occupied by the heating arrangements and the rooms necessary for the other operations. In the middle of the building is a staircase leading from the lower to the upper floor, and situated between two solid walls which reach from the foundation to the roof and form the inside longitudinal boundary of the stacks. Two or three rows of strong wooden boxes are placed one beside the other inside the stack, leaving gangways about five feet wide between them. The bottoms of these boxes generally rest directly upon the flooring of the beams aforesaid. The gangways between the boxes are boarded with strong planks fastened down in the same way as ordinary flooring-boards. The gangways are, of course, arranged to afford easy communication between themselves and with the door.

The dimensions of the boxes which are intended to receive vinegar and the skins of pressed grapes depend on those of the stacks themselves, so that no exact details can be given. They must, however, be as strong as possible, and perfectly staunch, to prevent leakage and loss of acetic acid. They must also be provided with very strong lids, fastened in such a way as to leave a sufficiently large opening for charging the boxes with the above-mentioned materials and for emptying them. Each box is surrounded on three sides with a board partition reaching to the top of the stack, so that each chest forms the bottom of a separate chamber, one side of which is left, for the most part, open to the gangway. These chambers are fitted with smooth planed wooden racks like drying-racks (see Fig. 32), on which the leaden strips are suspended.

Since the racks rest partly on the lids of the boxes and have to bear a very considerable weight, it is absolutely necessary, as already mentioned, that these racks as well as the lids should be correspondingly strong. The aforesaid opening in the lid—in some works several of these openings are provided, but without any noticeable advantage—is provided with a properly fitting wooden lattice. By this means the white lead, falling down from the racks and often collecting in considerable quantities on the top of the lids, is prevented from dropping into the boxes. When, as is mostly the case, a mixture of vinegar and spent grape husks is used, a 1½ to 2 inch hole must be bored in the bottom of each box and closed by a suitable wooden spigot. In emptying the boxes any residual acid liquor is drained off through this hole, on withdrawing the spigot, into a vessel underneath. Since the mixture contained in the boxes has to be stirred, every chest is provided with a stirring device the shaft of which projects through a hole in the side of the box far enough to enable the fermenting material to be stirred effectually from the gangway.

Of late certain improvements have been made in some of the white lead works still manufacturing by the Klagenfurt process, which, as we have already seen, is defective in many ways These improvements primarily relate to the construction of the lid, which is provided with a single opening, and has the shape of a low pyramid. Around this pyramidal elevation—which has, in addition to the lattice-covered opening at the top, a large number of lateral holes for the escape of acetic acid and carbonic acid—are fixed the frames for the leaden strips. The top of the pyramid can be taken off, leaving a larger hole which greatly facilitates the emptying of the boxes. Moreover, the special shape of these lids prevents the accumulation of white lead droppings, and keeps these from falling into the boxes.

At one time very primitive devices were used for heating the boxes—for instance, long and disproportionately broad brickwork flues below the chests, and in most cases from a furnace outside the workroom proper. This, of course, prevented the regulation of heat in the manner desirable for carrying on the process properly, even when the men in charge of the heating were able to see from certain indications that the temperature was fluctuating. At present the best-equipped works are fitted with efficient heating appliances enabling a constant temperature to be maintained both in the lower room and in the stack. Great stress is now laid on the thorough heating of the lower room, which must therefore be correspondingly strongly built, the heat being conducted through special flues into the upper room. In such case all the temperature controlling devices necessary can be easily fitted up.

The strips of lead to be treated by the Klagenfurt process are of somewhat different shape to those in the Dutch process, being not only broader but also far thinner. The selection of this shape was based on the assumption that the formation of white lead must proceed more rapidly and vigorously the thinner the metallic lead coating and the larger the working surface exposed to corrosion by the acetic acid and carbonic acid employed. For this reason, in making the leaden strips they are not cast into moulds, as described in connection with the Dutch process, but the molten metal is ladled out in short jerks over an oblique polished iron plate, the metal then cooling to a coating about the thickness of stiff packing-paper. Made in this manner, the thin leaden sheets are naturally very irregular at first, and therefore when cold they must be cut with shears into strips of uniform length and breadth. The trimmings are returned to the melting-pot.

The corroding boxes having been filled with vinegar and fermentation materials, the strips of lead foil are hung over fairly round thick wooden rods, so as to be at equal distances apart and to have both ends hanging down the same length. The rods are then put on the racks above the fermentation boxes, care being taken to keep them a certain distance apart. When the spaces above the boxes are all filled with the lead strips, each chamber is shut off from the gangway by a loose door fitted with a readily movable slide opposite the opening of the box lid.

When the walls of the closed rooms have been examined for leakages, and any faulty places have been repaired, the heating of the boxes may proceed. As the temperature rises, the process of forming white lead will begin, and thereafter keeps pace with the regular supply of heat. The duration of the process depends on a number of very different circumstances, the slow progress of the fermentation process itself being primarily responsible for the protracted corrosive reaction.

To explain the chemical process of the Klagenfurt white lead method, it must be assumed that under the gradual influence of heat the saccharine wine residues in the working chests are subjected to an alcoholic fermentation whereby, in addition to alcohol, a considerable amount of carbon dioxide is produced. The alcohol is converted into vinegar by oxidation and heat, either at the moment of formation or afterwards, the vinegar being partly evaporated. Owing to the delay in starting this fermentation process, it is necessary, in order to begin the corroding process, to supply the chests at the outset with a certain quantity of vinegar, which vaporises and acts on the metallic lead, thus forming basic lead acetate. Later on, when fermentation begins, carbonic acid is liberated in a sufficient quantity to convert the basic lead acetate into white lead. Since, however, the formation of carbonic acid will cease when the sugar content of the fermentation materials is exhausted—in which case the formation of white lead will also cease for lack of carbonic acid – it becomes necessary to renew the fermenting material from time to time in order to maintain an uninterrupted production of the basic lead carbonate. For this purpose the boxes must be partly emptied, and refilled with suitable material as soon as the existing charge has become spent. This operation must be repeated as often as necessary until all the lead has been completely transformed.

Formerly the circumstance that the Klagenfurt method furnishes a whiter product than the Dutch was ascribed to the superiority of the method itself. This supposition is, however, only partly correct, for though it cannot be denied that the application of naturally pure fermenting materials that do not, like dung, produce gases containing sulphuretted hydrogen is likely to yield the whitest product, yet the purity of the lead used is the chief factor in the operation. Now, Austrian lead has long enjoyed a high reputation for purity, and it is to this circumstance that the superiority of Klagenfurt white lead is due. This is confirmed by the fact that where a different kind of lead has to be used the results are often less favourable than when Austrian lead is available.

The successful application of artificial heat in the production of white lead indicated the possibility of introducing ready-made vinegar into the chambers instead of employing the slow fermentation method, which possibility was greatly facilitated by the invention of the quick vinegar process of Schützenbach, Pfund, and others. Later on, the invention of producing acetic acid by the dry distillation of wood opened up a source of cheap acetic acid in nearly unlimited quantities, and paved the way for the general introduction of the chamber process, which, owing to the application of technical improvements, has now attained to a very high degree of perfection.

The German chamber process was first successfully introduced by *Dietel*, at Eisenach, who may be considered its real inventor It has an undoubted superiority over the Klagenfurt process in that, on the one hand, the perfectly white basic lead carbonate is produced in a considerably shorter space of time, whilst, on the other, a less pure form of lead than the aforesaid Austrian metal may be used without adversely affecting the result of the process. The most important point, however, is that this process affords a reliable means of regulating the production of the white lead according to the needs of the case and the judgment of the operator.

The buildings containing the white lead chambers are usually in two storeys, though single-storey premises are often used. According to the peculiarities of the climate, and still more so with regard to the difficulty of obtaining building materials, these buildings are built either of stone or wood, the latter being nearly always the case in Russia, for example. In two-storey buildings the white lead chambers are arranged on the upper floor, whilst the heating arrangements, the apparatus to cast the leaden strips, the pans for vaporising the vinegar, and the furnaces for producing the carbonic acid are situated on the ground floor.

In single-storey buildings the last-mentioned appliances are always placed in rooms in front of the white lead chambers, and have to be traversed before reaching the latter. In such cases the workrooms are always situated on a lower level than the stacks.

In the chamber process the arrangement of the stacks differs from the Klagenfurt method, and is much simpler. The stacks, several of which may be combined in one building, vary, according to the size of the works, from 7-11 yards in length, 5½–8½ yards in breadth, and are at least 4½–5½ yards high. The roofs of the stacks may be flat or arched, the latter shape, however, being now very seldom seen. The walls of the stacks are constantly exposed to the influence of hot acetic acid and steam, and must therefore be made of or covered with some material capable of successfully resisting these influences. For this purpose a coating of plaster or a cement facing can be applied, though in course of time both materials will succumb to the aforesaid influences so far as to perish in places, crumble, and fall, thus contaminating the white lead. Latterly acid-proof earthenware plates have been used with great success for covering the walls, roof, and floor of the white lead chambers, these tiles being set in plaster of Paris. Such a covering will last for an indefinite time, and make up for the higher first cost by the smaller outlay on repairs as compared with plaster or cement.

A strong door of moderate height leads into the chambers from the outside, and must be kept shut during the process. Instead of a window, which is generally absent in stacks, there is a very low opening that can be tightly closed by a shutter. The assumption that continued exposure to light exerts an unfavourable influence on the formation of white lead lacks proof, and the absence of windows in white lead chambers must rather be ascribed to the endeavour to prevent any unnecessary lowering of the internal temperature.

The stacks are fitted with similar racks to those used in the Klagenfurt process, consisting of a large number of upright beams set in rows and reaching from the floor to the ceiling. These beams are connected by laths arranged in one direction (from the door to the opposite wall) in the form of a ladder. The square posts are set about 60–80 inches apart, and the laths are nailed on about 20–24 inches apart. In charging the stacks with lead these laths serve the purpose of supporting round rods about 6–7 feet long on which the lead strips are hung. The point to be considered in fitting up the racks is how to accommodate large quantities of lead without any waste of room, and to see that they are arranged in such a manner that by working backwards one rack after the other can be filled with strips without difficulty. A small space will be left very close to the door, and from this place the progress of the corroding process can be observed from time to time.

The acetic acid is supplied to the chambers in the form of vapour, produced by heating strong diluted vinegar in iron or (more rarely) copper pans, the vapour being led through stone flues or acid-proof earthenware pipes underneath the chambers and thence upward.

On entering the chambers the vinegar vapour traverses an upright earthenware glazed cylinder about 18 inches in diameter, situated in the middle of the floor and perforated with a number of holes about an inch in diameter. The cylinder has a domed cover which is also perforated. This arrangement distributes the ascending vinegar vapour uniformly through the chamber in all directions. It is advisable to conduct the vinegar vapour in earthenware pipes throughout, and these can now be obtained cheaply of any required dimensions. They have the advantage that owing to the upward slope of the pipe any condensed vinegar vapour flows back into the pan, which can scarcely be done when stone flues are used, so that the latter are a source of waste.

The arrangement of the pans for vaporising the acetic acid is nearly the same in all white lead works. The cast-iron pans generally used are provided with a dome of copper or earthenware, and are built into a furnace, with grate and ash-pit, in the usual manner. On the dome is a short length of wide bent pipe, with which the pipes leading into the chambers are connected in a suitable manner; a closable opening for pouring in the vinegar, if required, is also provided.

The carbon dioxide is generated by burning charcoal or coke in ordinary iron stoves, care being taken to ensure perfect combustion of the fuel, since otherwise the purity of the resulting white lead may be injured by the smoke and soot reaching the chambers. The most suitable stoves are generally small, charged with fuel at the top, and well arranged to secure a good supply of air. The product of combustion, carbon dioxide, is led off in ordinary stove-pipes either directly into the dome of the vaporising pan or else to the above-described earthenware cylinder, thus allowing the carbon dioxide gas to mingle with the vinegar vapour and pass through the openings of the cylinder into the chambers.

The exhaust flues of the stoves are fitted with an arrangement for cutting off the supply of carbon dioxide, namely, a close-fitting throttle-valve which diverts the gas through lateral pipes direct into the open air or into the chimney stack.

To supply fresh air to the chambers, if necessary, the floor or the lower parts of the walls must be provided with openings, fitted with ordinary clay drain-pipes, pointing downwards, communicating directly with the outside, and closed on the outer end with a sheet iron lid. The air draught is regulated as required by suitably raising these lids.

The lead strips are made in the way described in dealing with the Klagenfurt process, but since a far greater quantity of lead is required, the work is accelerated by using several iron plates, over which the liquid metal for making the strips is poured. By dividing the work in this way two fairly experienced workmen will be able to cast a very considerable quantity of lead into thin sheets in three or four days, and trim them into a suitable shape by cutting.

The quantity of metallic lead that can be put into one chamber depends on the dimensions of the latter. It may be assumed that in a works arranged on the usual plan, 6 to 10 tons of lead must be placed in a chamber of medium dimensions in order to secure profitable results. In very large works a single chamber will sometimes hold double the quantity.

It being essential to the success of the corroding process that there should be an uninterrupted circulation of the vapours of vinegar as well as of carbon dioxide and introduced air, a provision will have to be made for this by leaving a sufficiently wide distance between the metal strips. In the same way care must be taken that the rods over which the lead strips are hung are placed at a sufficient distance apart in all directions to allow of a proper circulation and consequently an effective contact of the gas and steam with the surface of the metal. When the white lead chamber has been fully charged with metallic lead, the door and the window openings must be shut tight, the lid of the air pipe taken off, and the vinegar vapour admitted. During the first days of the process only vinegar vapours and pure air are admitted into the white lead chambers, so as to form basic lead acetate, and not until it has been ascertained that this compound has been formed in sufficient quantity on the surface of the lead strips are the stoves for the carbon dioxide set to work.

Since the formation of a high-grade white lead, *i.e.*, one free from more than a small quantity of neutral lead carbonate depends on the presence at this stage of a really basic lead acetate, attention must be concentrated in supervising the chemical process in the corroding chambers, on securing the formation of the basic lead compound exclusively. This, however, is a matter of extraordinary difficulty if the acetic acid is allowed to act too energetically on the metallic lead, especially at a high temperature and without a sufficient supply of air.

For this reason one cannot be too careful in determining the proper degree of concentration of the acetic acid to be evaporated. In starting the process a stronger vinegar must be used; but in the same proportion as the temperature rises in the chambers and the action of the acetic acid on the metallic lead becomes more energetic the succeeding additions of vinegar must be weaker, to slacken the reaction. Thus if a vinegar of 5-6 per cent. strength be used at the beginning of the process, vinegar added the second day must be diluted five fold, and that used on the third and following days with at least an eight-fold or ten-fold quantity of water.

Before beginning to introduce the carbon dioxide, it is necessary to ascertain how far the formation of basic lead acetate has advanced in the chambers. For this purpose the chamber must be opened on the third day of the vinegar reaction, to examine the surface of the lead strips. If distinctly perceptible drops are observed thereon the carbon dioxide can then be admitted, but care must be taken first to reduce the admission of atmospheric air by about one-half. If, however, the drops upon the surface of the lead strips are so large as to run together on the slightest vibration, the supply of air must be shut off altogether for the present, and carbon dioxide introduced at once, though without interruption to the supply of vinegar vapours. With the admission of carbon dioxide in the chambers, the formation of white lead on the strips of lead begins, and the operation will now progress so quickly that in the course of a few days all the metal strips will be covered with a thin white coat.

One of the chief rules to be borne in mind in the management of the white lead process is that the atmosphere in the chamber must not be kept too dry. This will very easily happen if the supply of carbon dioxide is not in proportion to that of steam and acetic acid vapour, *i.e.*, is admitted in excess. Excessive dryness in the chambers can be detected at once by the coats on the lead strips no longer exhibiting a pasty or merely damp feel, but forming a hard dry crust, which can be flaked off partly in conchoidal bits by the finger-nails. This is a certain sign of excessive dryness in the stack, and being inimical to the successful course of the process, must be prevented at all hazards. This is easily done by interrupting the supply of carbon dioxide in due time, and for several days introducing fresh air into the chamber. By this means the temperature, which has risen too high owing to the heat furnished by the gas-producing stoves, will be gradually cooled, and sufficient moisture will soon be formed by the constant influx of steam and vinegar vapour.

The formation of white lead in a damp state is moreover desirable to prevent the dissemination of the highly injurious dust. The absence of moisture, as we shall see further on in connection with the Dutch process, constitutes a serious drawback to that method.

A further characteristic, indicating an irregular course of the process in the chambers, is the appearance of granular masses of white lead sometimes observed upon the metal strips. As their formation can be more especially noticed close to the earthenware cylinder, where the temperature is highest and activity of the vinegar and carbon dioxide most pronounced, the inference is that the supply of gas and vapour to the chambers is excessive. Therefore in such case the supply of carbon dioxide should be interrupted at once and that of the acetic acid diminished, and at the same time fresh air should be admitted freely. The admission of vinegar vapour may be resumed after a time and gradually increased until the normal course of the reaction in the chambers is restored, whereupon the air pipes should be closed and carbon dioxide readmitted. The natural course of the white lead process in the chambers depends on the preliminary formation of basic lead acetate, which is then converted into true white lead by the admission of due proportions of carbon dioxide and atmospheric oxygen. The neutral lead acetate formed as an important by-product reacts in turn on the metallic lead in presence of water vapour and forms new quantities of basic lead acetate, which latter is decomposed by carbon dioxide, and so on. As this theory is in accordance with the facts, it furnishes a basis for all the rules which have to be considered in the management of the chamber process, of which we have discussed the most important ones so far as outward manifestations are concerned. This theory of the formation of white lead also affords a simple explanation of the various phenomena observed.

In the first place, the current and essential practice of introducing at the beginning of reaction vinegar eight or ten times as strong as that used in the next stages of the process is very clearly explained. The formation of fresh portions of lead acetate through the precipitation of the already formed basic salt by means of carbon dioxide naturally requires a far smaller quantity of vinegar for maintaining the progress of the manufacturing operations.

On the other hand, the theory affords a means of properly judging the part performed by the carbon dioxide and the accompanying heat, as well as by the atmospheric air admitted from the outside. In managing the process then these only need be considered when they exist in considerable excess in the chambers, in which case the continued formation of basic lead acetate is greatly retarded, if not abrogated altogether, on account of the deficiency of the necessary moisture, and the whole process will naturally come to a standstill. This is the more likely to occur because the introduction of atmospheric air in the normal course of the manufacturing process is preferably limited to the quantity which enters the white lead chambers with the vaporised vinegar. Probably a very slight excess of heat is sufficient to cause a slackening of the chemical process; and the fact that the chambers are quite shut in prevents this fault from always being detected in due time.

To make sure that the chemical process is going on properly it is necessary to enter the chambers frequently. This entails the observance of certain special precautions on account of their very high temperature (up to 80° C.) and the presence of considerable quantities of carbon dioxide and vinegar vapour. For the purpose of this inspection therefore special protective clothing must be worn, together with an apparatus for artificial breathing; and as the chambers are without windows, it will be advisable to carry a lamp unless the doorway admits enough light. The time required for the complete formation of white lead in the chambers varies considerably. When the process has pursued a normal course, and remained free from any considerable interruption, a period of six (more rarely seven) weeks will be sufficient for completion, which will, of course, depend on the dimensions of the chambers and on the more or less practical arrangements for heating. If it be found on entering into the chamber, two or three weeks after the beginning of the work, that those metal strips most exposed to the influence of the acetic acid and carbon dioxide—*i.e*, those at the bottom—are already covered with a coating of white lead to such an extent that only a small core of metal is left, then the further successful progress of the work may be anticipated. This progress will be the more rapid from below upwards, since the under portions gradually fall to the bottom and thus afford the gases readier access to the rest. Finally, when the latter are corroded to such an extent that they tear at the slightest touch and fall down, the process may be considered as finished. The heating should then be stopped and the chambers opened, whereupon they will cool down in a short time.

On entering the chambers later on, the white lead will be found mixed with unchanged portions of metallic lead, mostly in the form of a loose mass, pasty in parts, which is collected with wooden shovels and conveyed to other rooms for further treatment.

c. *Finishing Processes*

In the state in which it leaves the corroding plant the white lead, no matter whether made by the Dutch, Klagenfurt, or German process, is not in marketable condition, and therefore has to be subjected to several finishing operations to impart to it the required shape or fineness. The first of these manipulations is for the purpose of separating the metallic lead still contained in the crude white lead, and transforming the white lead into a purer, more homogeneous mass. The purpose of the next operation, which is of the greatest importance, especially for the recovery of pure white lead as a fine powder, is to remove the neutral lead acetate by washing. The third and last operation is the shaping (grinding, sifting, pressing into small cones, &c.) of the washed (or merely levigated) white lead.

Whereas attempts were formerly made to remove the white lead (obtained by the Dutch process) from the unchanged residue of the lead coil by simply beating it off with a wooden mallet, special machines for this purpose are now used; for instance, those of Lefebre, Horn, and others. These enable the unhealthy task to be performed much quicker, and also, by the use of hermetically closed vessels, minimise the formation of dust, which is specially injurious to the workmen. The machines used for this purpose are generally built on one and the same principle, and consist of two or more fluted iron rollers, through which the coils or strips of lead covered with white lead are passed. The pressure of the revolving adjustable rollers on the white lead crust, which is very seldom deposited in a loose or pulverulent form on the metal, causes the crust to split off in scaly splinters, which fall into a chest underneath, whilst the metal strips leave the apparatus on the other side. By reason of the quiet and uniform motion of the rollers the formation of dust, inevitable in beating by hand, is greatly diminished, and the dissemination of the poisoning dust prevented by the use of tightly closed apparatus.

The loosened white lead was formerly put on the market under the name "slate white" without any further finishing; and this quality of white lead was considered as possessing specially high properties with regard to purity, whiteness, and covering power. In fact, adulteration with barytes or other adjuncts which would spoil the shaly fracture of the pure colour was out of the question. This alleged superiority of slate white over other white lead brands is, however, open to question.

The white lead obtained by the Dutch and Klagenfurt processes must be ground down uniformly with water, unless, as rarely happens nowadays, it is wanted in the form of "slate white." Formerly this treatment was carried on exclusively in wet mills, constructed on the same principle as shown in Fig. 43 *et seq*, except that the wooden casing was made considerably lower, and the feed opening in the upper millstone was provided with a sheet-iron hopper. In large works 9-12 such wet mills were fixed in a row, and divided into sets of three mills, each set having to treat a certain quantity. The ground material, issuing from the first wet mill, was transferred to the next one, and after having passed through it, to the third one, after which it was generally considered to be sufficiently fine. Later on the wet mills were arranged in steps, one above the other, the material issuing from the top one being delivered direct into the next one below, and from this on to the lowest. At present this type of wet mill is very rarely used, these being replaced by cylindrical mills, like ball-mills, lined with porcelain plates and provided with balls of the same material or round stones. These mills have the great advantage of preventing any contact between the white lead and iron fittings, and of grinding much quicker and finer than the older form.

White lead made by the German chamber process cannot be separated from the metallic lead in the same manner as described above, because the mass coming from the chambers is always more or less damp. In this case, therefore, the separation must be effected by a kind of levigating process by means of pure water, which can be performed in a variety of simple ways. For this purpose use is generally made of a large copper cylinder provided with a perforated jacket and a tight-closing feed opening through which the mass is admitted and the residual lead removed after the pigment has been washed off. The drum revolves in a watertight tank, provided on one side with a water inlet and on the other an outlet, the whole arranged so that at least one-third of the jacket surface is always under water. The working of this apparatus is very simple and easy to grasp. The continual rotation of the drum keeps the mass in constant movement, whilst the uninterrupted admission of fresh quantities of water gradually washes off the white lead (which adheres only slightly to the lead strips), distributes it in the water, and carries it away into tubs either placed directly underneath the apparatus or connected with it by a suitable gutter. By this means only the finest particles of white lead escape, the coarser parts settling down to the bottom, by reason of the high specific gravity of the pigment. When no more white lead issues from the drum, the latter is emptied and recharged, whereupon the same procedure is repeated. The coarser white lead in the bottom of the apparatus itself must be emptied from time to time, and ground in wet or ball mills as fine as possible, in the same manner as the product of the Dutch or Klagenfurt process. When the required degree of fineness has been attained, the pigment is mixed with that in the tubs, and the mixture is finally washed with pure water, in the usual manner, until all or most of the neutral lead acetate has been removed. The absence of this compound can be easily tested, on treating a filtered sample of the washing water with diluted sulphuric acid, by the non-appearance of precipitate beyond a slight cloudiness. The washed white lead is pumped into filtering presses or, where these are not available, filtered in baskets, pressed in an ordinary box press, dried, and finally ground to a fine powder in a ball-mill fitted with a sifter.

The washing waters, still containing a considerable quantity of neutral lead acetate (sugar of lead), are generally treated for the recovery of that substance. These washings are run into pits, where the sugar of lead is precipitated with a solution of sodium carbonate or ground chalk. The reaction furnishes lead carbonate, together with sodium acetate or calcium acetate, both in solution and easily separable from the precipitated lead salt. According to the degree of care taken in collecting the washings and keeping the reservoirs perfectly clean, a more or less pure lead carbonate will be obtained, though it will rarely be pure enough to be fit for mixing with a good quality of white lead, and is therefore generally used as an adjunct in inferior brands. To make cheap brands of white lead (Venetian white, Hamburg-Dutch white lead) the genuine article is mixed with barytes, or more rarely with other materials. Of course only an absolute white and very finely ground barytes can be used for this purpose, otherwise the pure shade of the white lead will be affected. The barytes can be added either dry or in the wet state.

If the pasty white lead is to be formed into small cones, it may either have been completely washed beforehand or still contain a portion of the surplus sugar of lead. The washed white lead is generally so hard that there is little risk of the cones breaking in pieces when dry, even when the white lead is mixed with barytes. The cones, however, are harder and brighter in proportion to the amount of sugar of lead present in the white lead paste used. The same is the case with Krems white, which differs from the other only in its shape (square or rectangular tablets, 1 1½ inches thick). To increase the durability of the cones, the damp paste may be mixed with a thin gum or flour paste.

d. The French Process (after Thénard)

When carbon dioxide is passed into a saturated solution of basic lead acetate, $Pb(C_2H_3O_2)_2.2Pb(OH)_2$. two molecules of lead will be precipitated as white lead (basic lead carbonate), whilst neutral lead acetate remains in solution. This solution of sugar of lead, on being treated with litharge and warmed, takes up a certain quantity of that body and forms a fresh quantity of basic lead acetate. When this is treated with carbon dioxide, the first reaction is repeated, white lead and neutral lead acetate being formed, which latter can be saturated again with litharge, and so on.

This mutual reaction between basic lead acetate and carbon dioxide on the one hand and sugar of lead and litharge on the other was made known by Thénard in 1801. Brechot and Leseur, and later Roard, of Clichy, used it for producing white lead in factories, and their process, which was first carried on in France, is now always known as the "French white lead process."

Although far more rapid than those already described, and furnishing a much whiter product, the French white lead process has not made such headway as the German process, for instance, for reasons already detailed in the Introduction. Since basic lead acetate is used as the raw material in the French white lead process, we will consider this substance first. There are three ways of producing basic lead acetate—viz., by treating (*a*) metallic lead with a corresponding quality of pure acetic acid; (*b*) the metallic lead may be replaced by litharge, lead oxide; and (*c*) an aqueous solution of crystallised sugar of lead can be boiled with litharge until it is completely saturated—*i.e.*, converted into the basic compound.

It is an essential condition for obtaining a pure white basic lead carbonate that a perfectly pure vinegar be used for producing the basic lead acetate, no matter if litharge or metallic lead be employed. It will therefore be preferable to employ crystallised sugar of lead from the beginning if it can be obtained cheaply, since it is very rarely adulterated to any extent.

To dissolve metallic lead in acetic acid without difficulty or loss of time it is first necessary to convert it into the most suitable condition for dissolving. The best form for this purpose is granulated lead produced by pouring the molten lead through a flat sieve into cold water. The metallic lead thus prepared is treated in the following manner: A wooden tub of medium size, 5 ft. high inside and 4-4½ ft. in diameter, is fitted at about 10-12 in. above the bottom with a false bottom perforated with a great number of holes of the size of a pea. On this false bottom the lead granules are piled up loosely, so as to allow constant and free interstitial circulation of air. Above the true bottom the tub is provided with an outlet through which the liquid contents can be run out if required into a collecting tank placed directly underneath the tub. In large works the dissolving process is accelerated by surrounding the collecting tank (which must be correspondingly larger) by a number of other tanks of equal size and fitted with the false bottom arrangement described. Care must be taken to leave enough space between the single tanks to enable the necessary operations to be performed without hindrance. Solution will not be properly effected unless a sufficient quantity of atmospheric air be admitted, the atmospheric oxygen generating heat and oxidising the metal, thus facilitating the dissolving process. To ensure normal progress of the operation this circumstance must be very carefully borne in mind, and for this purpose the following method is the best: The lead granules in the tank are gradually suffused with enough acetic acid to finally cover them entirely. After about half an hour, during which time the liquid has been left at rest in the tank, it is run off completely into the lower collecting tank, in which the oxidation of the remaining metal still moistened with vinegar will mostly begin at once. In proportion as oxidation progresses, the attendant evolution of heat will increase, the resulting progressive disengagement of hot vapours being a sure sign that the operation is proceeding successfully. When the temperature has reached a maximum—a condition easily ascertained after a little experience—the liquid in the collecting tank is poured over the lead granules again and left to react for about thirty minutes. Shortly after the liquid has been drawn off again a fresh oxidation of the metallic lead takes place with great evolution of heat, and at the proper moment the suffusion with the liquid from the collecting tank must be repeated. The whole operation is continued in the same manner until the solution of lead acetate has attained the proper concentration, *i.e.*, is completely saturated, and in a fit condition to be treated with carbon dioxide. The above described manner of working will of course be just the same when several tanks are used, but care has to be taken to keep the process continuous. The lead in the tank having been dissolved, except for a small remainder, the operation is interrupted, the tank emptied, and the lead residue, after being washed with cold water, added to the next charge of granules.

Dissolving litharge in vinegar or sugar of lead is a much simpler and quicker process, on account of the greater solubility of this compound, and for that reason this material is preferably used for making lead acetate in the French white lead process. The difference in price between metallic lead and litharge is very small and compensated by the saving in wages due to the easy and more rapid course of the dissolving process. In this case also the dissolving process is best effected in a spacious wooden tank provided with a copper or leaden steam pipe. The tank must be charged with the weighed quantity of vinegar or sugar of lead, pure water added, and steam turned on. When the dilute vinegar has attained a temperature of 50°-60° C., the finely ground litharge is added. When sugar of lead is used, this solution must boil briskly before the litharge is added, otherwise the latter settles down to the bottom and adheres so firmly as to be very difficult of removal. During the process the liquid must be kept thoroughly stirred. The litharge must not be added to the boiling liquid all at once, but gradually a shovelful at a time, and with a shaking movement, so that all will dissolve immediately. A slight excess of litharge is admissible, and in certain circumstances quite necessary, but the increasing concentration of the solution must be carefully tested throughout the process with a specific gravity instrument. The process is incomplete so long as the density continues to increase, thus indicating that the solution is able to take up a further quantity of litharge. When the density reaches a point at which it remains constant, the supply of litharge is stopped and the process is considered as finished, since any further addition of litharge would form basic compounds, solutions with a lower content of lead, indicated by a reduced density. Should this occur accidentally or through carelessness, the solution can be easily restored to the proper degree of concentration by adding a small quantity of vinegar or sugar of lead. The dimensions of the working tank being known, and the habit acquired of working always with the same quantities, a little care enables the completion of the reaction to be recognised without difficulty. The solution of basic lead acetate, whether obtained from metallic lead or litharge, must be clarified before use in a separate vessel, to effect the deposition of all extraneous substances.

In the French white lead process the production of carbon dioxide is generally carried on in the way described for the Klagenfurt and German methods. It is, however, essential that the gas admitted into the solution to be precipitated should be under a certain pressure, namely, equal to that due to the height of the lead acetate solution, or preferably somewhat greater. This pressure is obtained by aspirating the carbon dioxide by means of fans which deliver it after purification either into a gas-holder over water or else directly into the solution of lead acetate under treatment. In the former case it will also be delivered under a certain pressure, which can be regulated from the gas holder through staunch iron pipes, into the precipitation tank. These pressure devices must always be provided, whether the gas be natural carbon dioxide escaping from the earth (as it does in some places) or produced by artificial means. Nowadays, however, it is more convenient to use compressed carbon dioxide, conveyed in cylinders and obtainable from chemical works in a very pure state. This obviates the necessity for using the aforesaid mostly very complicated and therefore very expensive devices, inasmuch as the gas cylinders can be connected directly with the precipitation apparatus, the gas pressure in the cylinders being high enough to overcome the pressure of the column of liquid with ease.

The actual course of the precipitation process, as performed in well equipped modern white lead manufactories, is shown in Fig. 58. The wooden tank *H*, provided with a mechanical stirring machine, serves for the production of the basic solution of lead acetate from litharge and vinegar, or sugar of lead and litharge. This operation can be accelerated as desired by introducing direct steam through the pipe *R*. The finished solution is delivered through a tap into the clarifying tank *K*, directly underneath the tank *H*, and remains there until all the insoluble materials present have settled down to the bottom. While this is taking place the tank *H* is recharged with litharge and vinegar, to produce in the same way a further solution of basic lead acetate. From the tank *K*, which may be lined with good tinned sheet copper, the first prepared and now perfectly clear solution runs into

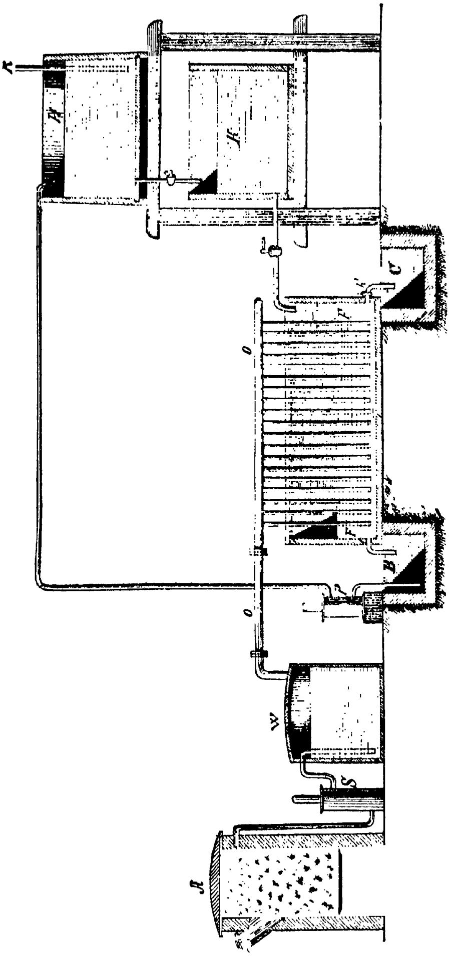


FIG. 58.

the precipitation vessel proper, a spacious vat *F* provided with a tight-closing lid, the tank itself being made of 2½–3 inch pine. A number of narrow pipes pass through the lid of the vat to the inside (in large works 600–800 of these pipes are used), all connected with the carbon dioxide main *O*, and dipping about 14–16 inches into the solution of lead acetate contained in the vat. When liquid carbon dioxide is used, the cylinder containing it is screwed on to the pipe *O*, so that on opening the valves the gas supply can be regulated according to wish. If, however, carbon dioxide generated by burning coke be used, there must be interposed between the generating furnace *A* and the pipe *O* a suction and force pump connected with a gas washer *W*, as shown in the sketch. According to the quantity of basic lead acetate or the dimensions of the plant, the precipitation and deposition of the white lead will be complete in 10–14 hours.

The carbon dioxide only precipitates from the solution of basic lead acetate the lead oxide present therein as base, and therefore any excess of carbon dioxide is useless as soon as the lead is all down. Hence to save expense the whole process must be controlled exactly by taking samples from time to time. As soon as the liquid in the precipitation tank begins to redden blue litmus paper, the precipitating process is nearing completion; and when the paper is permanently reddened, no further precipitation of lead by the carbon dioxide occurs, and the admission of gas should be stopped.

The precipitated white lead having settled down to the bottom of the precipitation tank, the supernatant clear liquid, consisting of neutral lead acetate, is run off into the vat *B*, from which it is returned to the vat *H* by the pump *P*. Here it is converted into basic lead acetate by adding a corresponding quantity of litharge. The precipitated white lead passes through the tap *h'* into the tank *C*, and is then separated by a filter press from the still adherent solution of neutral lead acetate which is added to the solution already in the tank *H*. The white lead can be effectually washed in the filter press itself, the washing waters being discarded as useless. The subsequent treatment of the wet white lead after it leaves the filter press is exactly the same as in the Klagenfurt or the German process.

The above-described precipitating vat may be replaced by a certain number of precipitation tanks provided with tightly-closed lids through which the supply of carbon dioxide into the basic solution of lead acetate is introduced by means of a pipe. This pipe is mounted in several coils close to the bottom of the tank, so that the carbon dioxide issuing through a large number of small orifices in the pipe is disseminated through all parts of the liquid under treatment. In continuous working, after the precipitation of the white lead in the first tank has been completed the carbon dioxide pipe must be connected with the coil in the second tank to carry on the precipitation process there while the precipitate in the first vat is having sufficient time to settle down thoroughly. The same method is pursued with the contents of the other tanks, so that the work is continuous.

Where liquid carbon dioxide is not used, it is essential to the health of the workmen that the whole plant should be installed in lofty, well-ventilated rooms. The carbon dioxide produced by burning coal contains considerable quantities of poisonous carbon monoxide gas, which takes no part in the precipitation of white lead, and will consequently escape into the workroom if the tank be leaky, and there produce most injurious effects. Hence, every precipitation tank must be provided with an outlet pipe leading off the carbon monoxide gas into the open air or a chimney stack.

In a manufactory at Lake Laach natural carbon dioxide issuing from the ground is used. It is pumped into the base of a tower about 12 feet high, where a strong solution of basic lead acetate is allowed to drip from the perforated ceiling.

If a filter press be available for separating the white lead from the neutral lead acetate, this operation may be performed, of course, on large filters, as represented in Fig. 10. The liquid passing through the filter is collected and worked up into basic lead acetate in the usual manner.

One hundred parts of lead should furnish about 129 parts of white lead, though as a rule the yield will not exceed 126–127 parts.

The drying of white lead is effected in two stages. First the wet material is put into pots which are laid on shelves in a large drying-room heated to about 30° C. This room is well ventilated by the draught of a chimney or by artificial means. In winter time the room must be heated, but in summer no artificial heating is usually needed. The drying process must be performed with care in order to prevent any breaking of the loaves of pigment in the pots, as would occur if heated too quickly, suddenly, or to excess. After some days the loaves are so far dried that they can be turned out by reversing the pots on to boards, the unbroken loaves keeping their shape. The drying is finished afterwards in another room heated to 50° C.

The loaves, cakes, &c., that have preserved their shape in drying are wrapped in paper at once and put on the market in this form, whilst such as are broken must be reduced to powder and sold as such.

To protect the workpeople from lead dust in handling the pigment, Büsing has constructed a drying channel-stove. In this stove the wet material coming from the filter presses is placed on a truck and passed through a flue heated to about 30° at the entrance and about 80° at the other end. In passing slowly through this flue the white lead becomes dry, and on reaching the farther end is discharged into a packing chamber which is hermetically closed except for a flue at the top. From the trucks the white lead is discharged into kegs, where it is rammed tight by a stamping machine. All this is effected without exposing the workpeople to injury from any development of dust.

Where this arrangement is not installed, the dust arising in the work of packing is drawn off by fans, and the kegs placed on a jigger to facilitate close packing, being also covered with damp cloths.

Max König of Alfeld has patented a special process for drying white lead (Germ. Pat. No. 137,907), which process, though rather complicated and requiring a large apparatus, also answers the important purpose of keeping the workpeople out of direct contact with the dry material. The charged cages of the filter press are conveyed mechanically into suitably arranged drying-chambers, and the dried colour is similarly transported to the storage vessels.

Apart from the processes already discussed, a number of proposals have recently been made for accelerating the manufacture of white lead. How far these proposals, however, really represent profitable manufacturing methods cannot yet be decided. It may, however, be assumed with some certainty that nearly all the proposals made for simplifying the manufacture of white lead give a product which (according to the theory of the chemical processes involved) consists only of neutral lead carbonate, and not of true white lead. This circumstance would probably bar the application of the methods in question, just as is the case with the French process.

That, in view of the manifold applications of white lead, earnest attempts have long been made to discover a cheaper and more practical method of production is not surprising. Nevertheless, no one has yet succeeded in turning out a product equal in all respects to that furnished by the Dutch process. For this reason the most important of these other processes may be dismissed with a few words.

Lead sulphate, a by-product of the Turkey-red process in calico printing, has been tried in different ways as a raw material for white lead. According to *Payen*, it can be treated with ammonium carbonate or sodium carbonate. whereby lead carbonate and alkali sulphate are formed. *Puissant* boils the lead sulphate with soda, carbon dioxide being introduced. The resulting products, however, are very unlike the real white lead in composition, not being basic compounds at all.

Pattison treats lead chloride with magnesium carbonate, and thus obtains a product consisting of lead carbonate and lead chloride. For decomposing the chloride a supplementary treatment with caustic soda is necessary, sodium chloride and lead hydroxide being formed, so that in this case a basic carbonate is produced.

According to *Bronners* (Germ. Pat. 52,262), lead sulphate is heated with caustic soda, thus forming basic lead sulphate. This when heated with sodium carbonate furnishes basic carbonate, for instance:

$$2PbSO_4,Pb(OH)_2 + 2Na_2CO_3 = 2PbCO_3Pb(OH)_2 + 2Na_2SO_4.$$

Montgomery of St. Louis has elaborated a process for manufacturing white lead, according to which molten lead and water spray are atomised in a closed chamber. The resulting mixture is next put through a mixing machine, then treated in a carbonating cylinder and finally ground fine.

Numerous and interesting experiments have been carried on for the electrolytic production of white lead, some of them with such apparent success that large plants have been erected to work these processes. In this case again, however, it has been found impracticable to imitate the composition and the qualities of white lead from the Dutch process by electrolysis, so that these methods have been abandoned.

White lead has been produced electrolytically both by the indirect and direct methods.

Browne and Chaplin use a solution of sodium nitrate of 10° Bé strength, which is electrolysed in a tank divided into two parts by a porous diaphragm. The positive pole is formed by a block of lead, the negative one by a copper plate. The electric current decomposes the sodium nitrate, forming lead nitrate at the positive pole and caustic soda at the negative pole. The mutual reaction of these two solutions furnishes lead hydroxide and sodium nitrate. The lead hydroxide is transformed by sodium carbonate into lead carbonate, caustic soda being liberated. The solution of the latter is treated with carbon dioxide, forming sodium carbonate for use over again. The greater part of the sodium nitrate being regained, the procedure, in which only the lead anode is consumed, is a very cheap and practical one.

According to *Tibbit's patent*, white lead is obtained direct by electrolysing a mixture of sodium nitrate and ammonium carbonate with a lead anode, and introducing carbon dioxide during the process. The precipitated lead hydroxide is thereby transformed into lead carbonate.

Oettli electrolyses a 1 per cent. solution of common salt with lead electrodes; the precipitated lead hydroxide takes up carbonic acid from a current of that gas traversing the bath, and is converted into lead carbonate, sodium chloride being re-formed. The precipitated lead carbonate is treated again with carbonic acid in another vessel.

The electrolytic process offers the advantage of continuous working and an extremely small amount of waste, and it also furnishes in a short time large quantities of an extremely fine and pure white product. Another advantage consists in the lead being used in the same form as it comes from the foundry without having to be remoulded. Finally, this process effects a considerable saving in space, material, and labour. Nevertheless, the grades of the white lead obtained by the electrolytic process are not equal in covering power and brilliancy to that from the Dutch process, and have not been able yet to displace this latter.

c. Properties of White Lead

According to its chemical composition, white lead consists of basic lead carbonate of the formula $2PbCO_3Pb(OH)_2$. The content of lead oxide varies in the different brands between 83·75 and 86·78 per cent., the carbon dioxide content between 11 and 16 per cent., the moisture content in the commercial product between 1 and 2½ per cent, from causes probably occasioned by the divergent methods of manufacturing. White lead has a yellowish white to pure white shade, is tasteless, devoid of smell, and has greater covering power than any white pigment at present known. It is quite insoluble in water, but in a pure state dissolves easily and completely in nitric acid or strong acetic acid with strong effervescence, caused by the liberation of carbon dioxide. Caustic soda, too, effects complete solution. Pure white lead is also soluble in very dilute or in boiling hydrochloric acid, but the solution deposits long acicular crystals, consisting of lead chloride, on cooling. Solutions of white lead give black lead sulphide with sulphuretted hydrogen or ammonium sulphide; sulphuric acid precipitates white lead sulphate; chromic acid throws down yellow lead chromate from a neutral solution.

On heating white lead to about 400° C. the contained carbon dioxide volatilises, lead oxide being left.

The percentage of carbon dioxide is determined in the finely-ground pigment dried at 105° C. with the Bunsen apparatus. To test the lead content, 2 grms. of colour are dissolved in 150 cc. of dilute hydrochloric acid at 50° C., a piece of bright metallic zinc being dipped in the solution. The lead reduced to metal in this way can be estimated direct by weighing.

With regard to covering power, the various brands of white lead exhibit very considerable differences, according to the method of production. In this respect the French white lead is decidedly inferior to the German article, and still more so in comparison with the Dutch product. On the other hand, it should be stated that the white lead produced according to the French process is purer and of a more brilliant shade than the Dutch white lead (which certainly has greater covering power), which very probably arises from the fact that the materials used for producing heat and carbonic acid in the latter process always disengage certain quantities of ulphuretted hydrogen and ammonium sulphide. As already mentioned, this divergent behaviour of the various brands of white lead is probably due to the larger or smaller percentage of lead hydroxide, $Pb(OH)_2$, and it must be assumed that the lower density of the French white lead, on which account it will take up more oil than the same volume of the German or Dutch product, also depends on this circumstance.

Sometimes white lead exhibits a pinkish tinge, caused by a slight trace of silver.

The inferior brands of white lead are usually mixed with barytes to cheapen the product; but this admixture cannot be considered an adulteration, provided it is not concealed from the buyer. In this case also fancy names, such as Venetian or Hamburg white, &c., are given to the article. Nowadays by far the greatest quantity of white lead is sold in a chemically pure state. In case of doubt whether a given sample of white lead is pure or adulterated with barytes, a small sample must be dissolved in diluted nitric acid. Should any residue be left in the solution after heating, it will be due to added barytes or some other adjunct insoluble in nitric acid. In addition to barytes and blanc fixe the following adjuncts are used: lead sulphate, zinc white, china clay, chalk and gypsum; and occasionally a little indigo is added to such mixtures to produce a very pure white.

In industrial applications white lead is almost exclusively used as an oil colour. To obtain a fine white coat of paint, exposure to the influence of sunlight, during and after drying, seems to be of special importance. This is proved by the fact that paintings done in white lead soon turn yellow, even in moderate darkness; but the original milk white shade will generally be restored if the yellow surfaces are exposed for a long time to light. Both in a dry state and as paint white lead is quickly turned black by sulphuretted hydrogen, black lead sulphide being formed. This disturbing susceptibility of white lead to sulphuretted hydrogen gas is the chief reason for the many attempts to find a substitute, all of them, however, without success up to the present. White lead that has not been sufficiently purified from adhering lead acetate has the sometimes troublesome property of making paint dry very quickly. A paint of this kind, containing about 6 to 7 per cent. of linseed oil, will on being kept get hard and lumpy, requiring protracted treatment to make it fit for use again.

It is very easy to ascertain whether white lead contains lead acetate by pouring a small quantity—about twenty to thirty grms.—into a porcelain basin with water, and heating it carefully over a flame, the whole being kept stirred. The liberated water vapour will have the characteristic smell of acetic acid and redden moistened blue litmus paper, owing to the presence of that acid. The aqueous solution will deposit a white precipitate of lead sulphate on the addition of sulphuric acid.

In spite of its absolute insolubility in water, white lead exerts a highly poisonous influence upon the human organism, on which account, especially in former times, when extremely primitive methods of manufacture were employed, the workmen suffered continually. Among maladies caused by lead the so-called lead colic is of most frequent occurrence. The first signs of this illness consist of pains in the abdomen, at first intermittent and in different places, but afterwards gradually localised and increasing in violence on account of the acute constipation, which resists all the usual remedies. The attacks are repeated at progressively shorter intervals, and are more violent at night than by day. At the same time the patient suffers from insomnia, great uneasiness, anxiety, convulsive difficulty in breathing, &c. Under suitable treatment and by scrupulous observance of the doctor's orders the colic soon passes away, but returns very easily, unless lead be shunned; and each successive attack is more difficult to cure. The sufferer being removed from the further influence of lead, the treatment consists in prescribing fatty and mucilaginous food, and beverages, especially milk. Acid food, particularly such as are prepared with vinegar, must be most carefully avoided.

The invalid must practise scrupulous personal cleanliness, bathing frequently, change the underclothing often, and be warmly clad. In specially difficult cases he must stay in bed for a long time. As an internal remedy opiates are given to lessen the pains; purgatives such as warm castor oil, calomel, jalap, senna leaves; and antidotes of lead, especially the various sulphur remedies. The external remedies for lead colic include more particularly oily and stimulating clysters, and sometimes a warm poultice on the body. By providing the workpeople with large quantities of warm milk at regular intervals during working hours and by frequently putting them to other tasks in rooms free from lead, the risk of an attack of lead colic can be considerably reduced, or, as is often the case in well-equipped works, avoided altogether.

In view of the danger of lead pigment to the human organism, some Governments have issued strict regulations* concerning the installation and management of factories for producing lead pigments and other products of that metal. These regulations are primarily concerned with the installation and arrangements of the work-rooms, female labour being prohibited except under certain conditions, and the employment of young persons entirely. The workpeople seeking employment must produce a medical certificate stating that they are neither weak nor suffering from complaints of the lungs, kidneys, or stomach, nor alcoholism. The workpeople must be thoroughly instructed on the danger of the work, and, in Germany for instance, must not be employed for more than eight hours a day. When working where lead dust is given off, the men have to be provided with caps, over-alls, respirators, &c., to be supplied by the master; and when working with solutions, the hands must be greased or gloved. The employer must have the state of the workers' health looked after by a physician. Workers who are ill or believed to be ill must not be kept at work. The number of hands, changes in the staff, and cases of illness have to be recorded in a book. Careful and minute instruction must be given to the hands about the danger and the available remedies, and these regulations must be strictly enforced.

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* In Germany by the law of May 26, 1903 —*Translator.*

f. Other White Lead Pigments

Besides the basic carbonate certain other white compounds of lead are used as pigments, though only to a small extent. Nevertheless, they will now be briefly mentioned here.

Pattinson's White Lead or *Lead Oxy-Chloride*, $PbCl_2PbO$, is made by precipitating a hot concentrated solution of lead chloride with a similar concentrated solution of caustic lime. The precipitation must be effected very quickly. The two solutions are allowed to run out simultaneously from pipes with lateral perforations, so as to mingle immediately and react, the compound thus formed falling into a collecting tank charged with a constant excess of lead chloride. In this tank the new compound settles down as a white powder. The supernatant liquor contains calcium chloride and the surplus quantities of lead chloride, the lead of which is precipitated as hydroxide on the solution being rendered alkaline by a further addition of caustic lime.

According to Pattinson, the native lead sulphide, PbS, used for producing this colour, is ground fine and boiled with hydrochloric acid. The sulphuretted hydrogen formed by this process is utilised simultaneously in the manufacture of sulphuric acid. The resulting crystallised lead chloride is dissolved in hot water after washing.

g. *Lead Sulphate. Non-poisonous White Lead. Mühlhausen White*

This colour is of dazzling whiteness, but has less covering power than the basic carbonate on account of its more crystalline nature. It is made by precipitating a soluble lead salt (acetate, nitrate in dilute solution) with dilute sulphuric acid, the dilute acetic acid obtained in the supernatant liquor being used over again for dissolving metallic lead. Lead sulphate is less used alone than for mixing with and shading other pigments. It is insoluble in water, and only very slightly soluble in acids.

Carten and Mariott grind litharge with one-fourth its own weight of common salt, and treat the mixture with sulphuric acid. Owing to the small importance of this pigment, there is no need to mention other more complicated methods of preparation employed.

Lead sulphate is obtained in large quantities as a by-product in the manufacture of aluminium acetate from lead acetate and alum, or aluminium sulphate, and in calico-printing works.

Neutral lead carbonate is put on the market as *silver white*; it is obtained by precipitating lead acetate with sodium carbonate.

Freeman's Non-poisonous White Lead is a mixture of lead sulphate, zinc white, magnesium carbonate, and artificial barytes.

Sublimed White Lead (*Bartlett Lead*) is obtained by roasting a mineral containing zinc sulphate and galena—lead oxide and lead sulphate being formed. The fumes containing these products and zinc oxide are collected in chambers provided for the purpose. The product obtained in this manner has to be subjected to somewhat complex treatment. The composition of the product is irregular; the shade is not pure, being a dirty grey tint. The covering power, however, is very high.

An apparatus for manufacturing white lead, representing a special improvement of the precipitating vessel, in which the finished product is separated from the liquid, has been patented by *Corbett* (Germ. Pat. No. 151,301).

IV. MANUFACTURE OF LITHOPONE

(*Charlton White, Enamel White, Orr's White, Griffith's or Knight's Patent Zinc White*)

The white pigment recently introduced into commerce under the name "lithopone" is a mixture of artificial barytes and zinc sulphide, and is claimed not only to replace the white lead hitherto used in all respects, but also to be superior thereto. Even though the expectations of many manufacturers in this particular have not been fulfilled by a long way, it cannot be denied that lithopone now enjoys a far more extended application than its opponents at first anticipated.

The first obvious difference between white lead and lithopone is the pure white shade of the latter, closely resembling zinc white Besides, it is specifically much lighter, and above all less dangerous to health than white lead. The most useful property of lithopone, especially for use as a constituent of paint, is that it is entirely unaffected by sulphuretted hydrogen. If made in the proper manner, its covering power, even if not greater (as is often asserted) than that of French white lead, will be very little inferior thereto. It does not, however, equal that of the German or Dutch white lead.

For producing lithopone, very finely ground barium sulphate (heavy spar, barytes, $BaSO_4$), as free from impurities as possible, is reduced in retort furnaces with coal to barium sulphide (BaS). The calcined product is treated with water, the barium sulphide being dissolved; and this solution is precipitated with a solution of zinc sulphate ($ZnSO_4$), the precipitate being washed, pressed, and dried. The dry mixture is afterwards calcined at a cherry-red heat, air being excluded, then granulated in water, ground in wet mills, and finally dried. In this state it is ground again in Excelsior mills, and is then ready for sale, being packed in kegs holding one to two cwts.

The barium sulphide obtained by the foregoing calcination process forms the raw material for the manufacture of nearly all the barium preparations already dealt with thoroughly in describing the manufacture of blanc fixe. The reduction process is explained by the following equation:

$$\underbrace{BaSO_4}_{\text{Barytes}} + \underbrace{4\,C}_{\text{Coal}} = \underbrace{BaS}_{\text{Barium sulphide}} + \underbrace{4\,CO}_{\text{Carbon monoxide gas.}}$$

The precipitation of barium sulphide with zinc sulphate proceeds in accordance with the equation:

$$BaS + \underbrace{ZnSO_4}_{\text{Zinc sulphate}} = \underbrace{BaSO_4 + ZnS}_{\text{Lithopone.}}$$

According to the recommendations of other manufacturers, the same result will be obtained by precipitating the barium sulphide solution with a solution of zinc chloride, zinc sulphide being precipitated and barium chloride left in solution. The latter is separated from the zinc sulphide and precipitated with zinc sulphate, thus forming blanc fixe and zinc chloride again, which latter can be used to precipitate barium sulphide once more. These transformations are explained by the following equations:

$$1.\quad \underbrace{BaS}_{\text{Barium sulphide}} + \underbrace{ZnCl_2}_{\text{Zinc chloride}} = \underbrace{ZnS}_{\text{Zinc sulphide}} + \underbrace{BaCl_2}_{\text{Barium chloride}};$$

$$2.\quad \underbrace{BaCl_2}_{\text{Barium chloride}} + \underbrace{ZnSO_4}_{\text{Zinc sulphate}} = \underbrace{BaSO_4}_{\text{Blanc fixe}} + \underbrace{ZnCl_2}_{\text{Zinc chloride.}}$$

The advantage of this method of precipitation is said to consist in furnishing the ingredients of lithopone separately, so that they can be mixed in any proportion to produce different grades of lithopone, whilst according to the first method the composition of the mixture is invariable. This method, however, has certain disadvantages, among them being the gradual accumulation of a quantity of more and more diluted zinc chloride solution, which is a source of considerable trouble. The manufacture of lithopone is divided in the following stages:

(1) The reduction of barytes (to obtain barium sulphide).
(2) The preparation of zinc sulphate.
(3) The precipitation of lithopone in a wet way.
(4) The calcination and finishing of the mixture of artificial barytes and zinc sulphide.

(1) *The reduction of the barytes*

with coal has already been discussed in connection with the manufacture of barium sulphate (blanc fixe), and can therefore be omitted here.

(2) *Preparation of Zinc Sulphate*

The zinc sulphate is preferably made on the premises by dissolving metallic zinc (zinc plate scraps) with dilute sulphuric acid. On account of the large volumes of hydrogen liberated in this operation, the apparatus must be placed in high, airy rooms, to allow the gas to escape unhindered. It must also be remembered that danger may arise from poisonous arseniuretted hydrogen when certain kinds of zinc dross and crude sulphuric acid (chamber acid) are used. In such cases, therefore, the ventilating appliances must be arranged with great care. The apparatus must also be arranged in such a manner as to prevent the accumulation of large quantities of hydrogen under pressure. Spacious oak tanks, provided with water and steam supply-pipes, are generally used. Directly above these tanks are placed earthenware, cast-iron, or leaden vessels, containing concentrated sulphuric acid, and fitted with valves in such a way that the flow of acid can be easily regulated. Three parts of metallic zinc require 4·3–4·5 parts of sulphuric acid (66° B.). The tanks are charged with a suitable weighed quantity of zinc scraps, a corresponding quantity of sulphuric acid being placed in the acid vessels. The tanks are next filled with cold water, the amount required being five times the weight of the zinc, which done, three-fourths of the necessary quantity of sulphuric acid is run in very slowly as a thin stream. In mixing the acid and water a considerable increase of temperature takes place, and the metal dissolves with brisk liberation of hydrogen. Excessive disengagement of this gas must be moderated by the occasional addition of cold water, which will check any overflowing of the strongly foaming mass. The liberation of hydrogen having diminished, the rest of the sulphuric acid may be added, steam being carefully introduced.

After twenty-four hours the formation of hydrogen gas will generally have ceased, and a portion of the resulting zinc sulphate will be visible in the form of crystals. When the zinc has been very impure, a good deal of sludge will usually be formed. In such case no residue of metallic zinc will be found, the extra weight of the impurities in the charge having disturbed the relative proportions of the acid and metal from the outset. A large quantity of cold water must then be added, followed by a suitable quantity of zinc scraps (not too much), and the whole boiled by turning on the steam until hydrogen gas ceases to come off. When a strip of blue litmus paper dipped into the liquid is no longer reddened, the boiling can be interrupted and the dissolving process considered as finished. The bulk of the impurities having been allowed to settle down to the bottom, the zinc solution is run off into the clarifying tank below the dissolving tank, and the residue in the latter is washed once with hot water. The washings, which contain a considerable quantity of zinc sulphate, are added to the liquid in the clarifying tank, whilst the zinc left undissolved is added to the next charge.

One of the chief conditions essential to the production of a faultless lithopone is that the zinc sulphate must be perfectly free from iron, since otherwise the resulting zinc sulphide would have a dirty appearance due to sulphides of iron, copper, &c. Since any iron present in a hot neutral solution will always be in the state of protoxide—the oxide being precipitated as a basic ferric salt—zinc sulphate must be treated with an oxidising agent before precipitating the iron. For this purpose bleaching-powder may be used, or (which is much cheaper) a thin cream of lime, milk of lime made from fresh-burned lime. This must be added until a filtered sample of the zinc sulphate solution gives a pure white precipitate when tested with lime, and not a brown deposit as before. When sufficient lime or bleaching-powder has been added, the solution is boiled up again by turning on the steam, the precipitate being then left to settle down thoroughly. The deposit consists of metallic residue from the zinc (lead, copper, &c.), ferric oxide, zinc oxide, zinc hydroxide, and gypsum. The best method of precipitating the metals contaminating the zinc sulphate is by putting long polished strips of zinc into the solution. This also gives the advantage that fresh zinc sulphate is formed by the mutual displacement of the metals in place of the decomposed sulphate of iron (or copper), so that there is naturally an increase of sulphate, and not, as in the lime process, a loss (in the form of gypsum).

When the solution of zinc sulphate is quite pure, its exact content of solid zinc sulphate must be determined before use, even if only to enable accurate calculations to be made. This can be done, for instance, by means of the hydrometer, as already described in the Introduction.

Roasted pyrites, too, containing zinc may also be used in the manufacture of zinc sulphate. These ores, after having been treated to expel about 30 per cent. of sulphur, still contain about 6–12 per cent. of zinc. Some lithopone makers treat such ores by mixing crushed ore with common salt and roasting in reverberatory furnaces. The zinc is converted into zinc chloride, sodium sulphate being also formed along with a certain amount of chlorides of iron and manganese. The solution obtained from the roasted material is but slightly contaminated.

The chief centre of the manufacture of zinc sulphate is the Lower Hartz district, where zinciferous lead ores form the raw material. Since the development of the lithopone industry this branch has made considerable progress.

(3) *The Manufacture of Lithopone by the Wet Method*

The precipitation of the solution of barium sulphide with zinc sulphate is usually performed in very large tanks. The barium sulphide from the calcination process is washed as already described in connection with the production of blanc fixe, and therefore the process and apparatus need no further mention here. The precipitation tanks for lithopone must be provided with suitable stirring appliances, since very large quantities have usually to be treated, and it will be advantageous, especially in large works, to erect several tanks in the one room, in order to accelerate precipitation. The process begins by pumping a certain quantity of barium sulphide solution (not exceeding about 5-8ths of the capacity of the tank) out of the clarifying tank into the precipitation tank, and then setting the stirring machine in motion. The solution of zinc sulphate is added until the transformation into barium sulphate and zinc sulphide is complete. To test for the presence of any excess of zinc sulphate or barium sulphide in the yellowish white liquid, a few drops are taken out, after protracted stirring, with a glass rod, and absorbed by white filter paper. The cleaned rod is dipped in a dilute solution of ferric chloride, and then applied to the edge of the drop on the filter paper. If the point of contact shows a black stain of iron sulphide, an excess of barium sulphate is present; but if the urine-yellow colour of the ferric chloride remains unaltered, the precipitation is complete, or at any rate zinc sulphate is in excess. In the latter event the sulphuric acid must be tested for with barium chloride. For this purpose a small quantity of the precipitate is filtered off clear, and treated with a few drops of barium chloride. The formation of a dense precipitate of barium sulphate indicates a considerable surplus of zinc sulphate. If only a faint turbidity is produced, the excess of zinc sulphate is very small, and the operation may be considered as finished.

If, however, the ferric chloride test revealed an excess of barium sulphide, a further quantity of zinc sulphate must be run into the precipitation tank, and the test repeated at short intervals until the yellow colour of the ferric chloride on the filtering paper remains unchanged. The above test with barium chloride is then applied. A slight excess of zinc sulphate is absolutely necessary, and on reaching this stage the white precipitate (now of a reddish tinge) is pumped, without interrupting the stirring machine, on to the filter presses, and washed with warm water until the washings no longer give a precipitate with barium chloride; or the stirring machine is also stopped to allow the precipitate to settle down in the tank itself. In this case the washing of the precipitated lithopone must be effected in the usual manner by repeatedly filling the tank with pure warm water until the washings no longer exhibit the sulphuric acid reaction. After filtering and pressing, the mass is cut in small pieces and dried on boards in heated drying ovens at a temperature of 48–50° C. In the dry state the lithopone forms a dull white, very hard body, which must be calcined before it can be considered ready for sale.

(4) *Calcining the Mixture of Barium Sulphate and Zinc Sulphide*

The crude raw lithopone is calcined in hermetically closed retorts. For this operation the furnaces used for the reduction of barytes in the manufacture of barium sulphide can be employed. Each retort is provided at the top with a sliding fire-brick plate for closing the gas outlet. The finely divided mixture is fed into the red-hot retort by means of long, trough-shaped shovels provided with short handles, and is spread to a uniform depth of about 3–4 inches. In ten minutes or fifteen minutes at the outside the mixture should have attained a cherry-red heat, and this moment having arrived, the glowing mass must be taken out of the retort with iron rakes and thrown into iron tanks filled about half full of cold pure water. The sudden cooling of the lithopone completely changes the structure. The pigment becomes softer and acquires greater covering power, whilst its appearance is quite unlike the white of the finished lithopone. This appearance is not restored until the cooled mass has been thoroughly ground in a wet mill. The grinding process is very troublesome, and takes at least 12–15, sometimes even 24, hours. The more thorough the grinding, the better the appearance of the dry lithopone, and therefore the operation must be very carefully performed. After the wet grinding the lithopone is filtered in filter presses or baskets, pressed, and dried in partly darkened rooms.

The subsequent dry grinding can be effected by ordinary mill-stones, or in any other kind of mill (*e.g.*, Excelsior mills).

Though lithopone is entirely unacted on by gases containing sulphur, it is to some extent sensitive to the influence of light, coatings of lithopone paint being found to darken and turn grey after exposure to daylight. This change has now been traced to the presence of small quantities of chlorine in the product. To obtain products quite free from chlorine, the process patented by the *Chemische Fabrik Marienhütte* proposes to free the crude zinc sulphate from iron and manganese by heating it with a permanganate and an alkali, the solution being then treated with zinc powder and copper sulphate, and dealt with in the usual way.

X. *Fischer* effects the same purpose in a similar way. The crude solution of zinc is treated with oxidising agents: sodium, potassium, calcium, &c., manganate or permanganate. The filtrate is treated with zinc dust, filtered again, and precipitated with barium sulphide solution.

This product, however, will not agree in chemical composition with the lithopone made in the ordinary way, but constitutes a mixture the relative proportions of whose components may fluctuate considerably. Practical experience has shown that the proportion of zinc sulphide is the most important factor in determining the covering power of the product, and therefore forms the chief criterion of the value of lithopone. In order to establish a trade standard in this respect, the manufacturers of lithopone have formed an association and classified lithopone into distinct brands according to the content of zinc sulphide. Thus in Germany the following brands are marketed :

Green seal, with 33 per cent. and more ZnS
Red seal „ 30 „ ZnS
White seal „ 26 „ „
Blue seal „ 22 „ „
Yellow seal „ 15 „ „

With regard to the content of ZnS a margin of 1 per cent. is always allowed. By working according to the formula corresponding to the fundamental equation :

$$ZnSO_4 + BaS = ZnS + BaSO_4$$

a product will be obtained with 29·4 per cent. ZnS, *i.e.*, the red seal brand. Lower qualities, that is to say, containing more $BaSO_4$, are produced by using sodium sulphate, soluble sodium sulphide being formed from the extra quantity of BaS employed. For instance, the white seal brand will be obtained from the formula :

$$5ZnSO_4 + Na_2SO_4 + 6BaS = 5ZnS + 6BaSO_4 + Na_2S.$$

In view of the low cost of the most finely ground and pure white barytes, it is unprofitable—at least in Germany—to produce the grades richer in $BaSO_4$ by the wet method, since the sodium sulphate is more expensive than the barytes. In such case, therefore, recourse must be had to mechanical mixing by adding to the normal lithopone corresponding quantities of very finely ground barytes, mixing them together in suitable stirring and grinding machines. This not only saves the expensive raw material, but also obviates the work of treating the mother liquors as well as the loss of time and work involved in washing and drying. The brands containing higher percentages of zinc sulphide will exclusively be produced by the wet method, green seal, for instance, according to the formulæ :

$$(a)\ BaS + Na_2S + 2ZnSO_4 = 2ZnS + BaSO_4 + Na_2SO_4,$$

$$(b)\ ZnSO_4 + ZnCl_2 + 2BaS = 2ZnS + BaSO_4 + BaCl_2.$$

The analysis * of lithopone has been dealt with recently by a number of chemists. The calcination and granulating processes decompose the zinc sulphide to a slight extent, and the zinc thereby liberated takes up carbon dioxide. This zinc carbonate, however, is not equal in value to the sulphide as a pigment. Hence if the whole zinc content of a lithopone be calculated as zinc sulphate, the consumer will be adversely affected, since the zinc carbonate will be given as sulphide. In the same manner the buyer will be prejudiced if the sulphide sulphur alone is determined, as in this case all sulphides added by accident or of set purpose will count as zinc sulphide. To be reliable, therefore, an analysis must give the weight of both.

Owing to the very different specific gravities of the two components, it may happen that the product is not quite homogeneous, and care is therefore necessary in sampling. Moreover, the analysis should invariably be performed on material dried at 100° C. until constant. $BaSO_4$ is found directly by weighing the residue insoluble in hydrochloric acid. A convenient and rapid method of estimating the zinc is by titration according to the equation :

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* Exhaustive papers on the analysis of lithopone have been published by Kochs and Seyfert in the *Zeitschrift f. angewandte Chemie*, 1902, p. 802; also by Drawe, *ibid.* p. 174.

$$2ZnCl_2 + K_4FeCy_6 + 3H_2O = Zn_2FeCy_6 + 4KCl + 3H_2O.$$

According to *Amsel*,* 50–75 cc. of the hydrochloric acid solution, filtered off from the $BaSO_4$, is treated with 1 cc. of 10 per cent. ferric chloride and 20 cc. of a 40 per cent. solution of neutral potassium tartrate, followed by neutralisation with ammonia and boiling, more ammonia being added if the solution is not clear. The hot solution is then treated with a standardised solution of potassium ferrocyanide until all the zinc is precipitated. This point is ascertained by treating one drop of the solution on a white porcelain plate with one drop of concentrated acetic acid (contact test), whereby an immediate faint blue stain of Prussian blue should be produced.

Lithopone is used solely as an oil colour, and has been known about twenty years.

Under the name *Sulfopone*, *Steinau* patented a product similar to lithopone, made from calcium sulphide and zinc sulphate. Calcium sulphide is obtained in a soluble form by boiling flowers of sulphur with a solution of caustic potash. A certain amount of sulphur is carried down in the precipitation process, and at a red heat escapes as a gas, thereby breaking up the mass and thus facilitating the further treatment. This product, consisting of zinc sulphide and calcium sulphate, is said to be softer and smoother than true lithopone.

Strontium in the state of sulphate has been introduced too into the combination instead of barium and calcium.

Alberti proposes a substitute for lithopone. He grinds zinc sulphate with chalk or with native barium carbonate (witherite), and calcines the mixture. The mass melts in the water of crystallisation of the zinc sulphate, and thus becomes intimately mixed, decomposing at a higher temperature to zinc oxide and calcium sulphate (or barium sulphate), whilst carbon dioxide is liberated. The fused product is granulated in cold water and finely ground.

The principal artificial white mineral pigments have now been described, but there are a few other products to be mentioned which are less used in practice at the present time.

Antimony oxide can be prepared by burning metallic antimony at a temperature somewhat above its melting-point, or by dissolving it in nitric acid. A cheaper method is gently to roast native antimony sulphide (antimonium crudum, grey antimony) in a finely powdered wet state in presence of air. The sulphur burns away as sulphur dioxide, and antimony remains as oxide. On dissolving native antimony sulphide ore in hydrochloric acid, sulphuretted hydrogen being liberated, and pouring the resulting solution of $SbCl_3$, after clarification, into a vessel containing a large excess of water, a dense brilliant white powder is precipitated; and this must be washed until all trace of acid has disappeared, the washing being then stopped to prevent decomposition. The pulverulent precipitate thus obtained is called *algaroth powder*, and has the composition $SbCl_3 + Sb_2O_3$.

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* *Farbenzeitung*, 1902, p. 42.

Mention should also be made here of *lead antimonate* and *lead antimonite*, both of which are fine white powders. Apart, however, from the trouble and expense of preparation, the defective covering power of these powders (due to their crystalline nature) prevents their use as pigments.

Bismuth white, basic bismuth nitrate, a brilliant white when fresh, is prepared by pouring a solution of bismuth in fuming nitric acid into a large volume of water. It is more sensitive than lead to sulphuretted hydrogen, and very difficult to use if only for that reason. It has been used for ages as a face powder, but is not altogether harmless, and is now replaced by *tin white* prepared in the same way (*i.e.*, by dissolving metallic tin in strong nitric acid and pouring it into water) as a dense heavy white powder, tin hydroxide, $Sn(OH_4)$. Though this product is not used as a pigment by itself, it is of considerable importance as a colouring ingredient in glass fluxes (opal glass) and enamels.

THE YELLOW MINERAL COLOURS

The following are the most important representatives of this group. They are applied to a large variety of technical uses at the present day.

1. *Zinc yellow*, a combination of metallic zinc with chromic acid. It probably has the formula $3ZnCrO_4K_2Cr_2O_7$ (*i.e.*, is a double salt).

2. *Chrome yellow*, neutral or basic lead chromate, which is put on the market in all shades, from the lightest lemon to the darkest orange, according to composition, and is considered the best of all yellow mineral colours for painting.

Litharge and the slightly yellow-tinted *massicot*, both compounds of lead and oxygen, with the chemical formula PbO, were formerly considered to be colours also, and partly used as such for painting. They are now, however, no longer taken into consideration as true colours, since, owing to their dull appearance as compared with chrome yellow (even allowing for the difference in price), similar shades can easily be more cheaply produced with earth colours.

All the yellow colours necessarily used before chrome yellow and zinc yellow were introduced are now manufactured in only very small quantities, partly on account of their high price, but partly too by reason of their inferior appearance. They are mainly employed as artists' colours, for which purpose they can hardly be replaced by others, owing to their absolute unchangeability under the most divergent influences. These are:

3. *Naples yellow*, consisting chiefly of lead antimonate.

4. *Cadmium yellow*, a sulphur compound of cadmium, of a bright shade, not inferior in brilliancy to the chrome yellows, is preferred as an artist's colour for its insensitiveness to the influence of sulphuretted hydrogen gas.

5 The so called *Cassel yellow*, probably of the formula $PbCl_2, 7\ PbO$, and now used to a smaller extent than any other yellow colour.

6. *King's yellow*, a compound of arsenic with sulphur (As_2S_3), which, owing to its being a poison, is used on only a very limited scale by artists.

7. *Indian or cobalt yellow*, a yellow crystalline double salt: $Co_2(NO_2)_6 \cdot 6KNO_2$.

8. *Siderin yellow*, also called *Mars yellow*, ferric chromate, $Fe_2(CrO_4)_3$, has received more attention of late than its slight superiority justifies.

9. The so-called *ultramarine yellow* (*lemon yellow*), barium chromate, of very little importance as a colour. The formula is $BaCrO_4$.

10. Tin sulphide, SnS_2 (known in the German trade as *musiv gold*), is now very little used, gradually being displaced by the products of the improved manufacture of metal-bronze.

The only colours important for technical purposes are those numbered 1–4, the manufacture of which will now be fully described, whilst that of Nos. 5–10 will only be summarised briefly.

(1) Zinc yellow (*Zinc Chrome, Zinkgelb, Jaune de Zinc*)

The application of zinc chromate as a yellow colour is of only recent date, and is not met with in trade to any great extent as a separate pigment, the greater part being employed for mixing with Prussian blue to produce the so-called zinc green. The shade of zinc yellow is not so varied as is the case with chrome yellow; on the contrary, when properly made, zinc yellow has a specially delicate and bright, rather light shade.

The application of zinc green has very largely increased of late on account of the very brilliant shades of green obtained with zinc yellow, especially as oil paints, and by reason of the very extensive range obtained by mixing the yellow and blue pigments. Hence the question of making a specially bright zinc yellow, of uniform composition and appearance, has grown very important. Whereas formerly zinc sulphate was used as the raw material, zinc oxide is now almost entirely employed for this purpose, and is in many respects more advantageous. In these circumstances the various older formulæ have become obsolete, and need not be discussed, especially since the products they yielded were of extremely poor covering power, and also too dark to furnish pure green shades when mixed with blue. The zinc yellow prepared from zinc oxide by the process which will be described later on has, on the other hand, a delicate, bright, primrose to sulphur yellow shade that cannot be obtained with the palest chrome yellows. This shade is, moreover, absolutely necessary for obtaining perfect zinc greens, distinguished by a characteristic pure green shade, in comparison with the so-called chrome greens (mixtures of chrome yellow and Paris blue) that approach more to olive greens.

Owing to the delicacy of the shades of zinc green, it is quite natural that the slightest deviation in the shade of the zinc yellow used for its production will be observed at once; and the difference is the more striking the darker the zinc yellow used. In such event the finished zinc greens, especially when ground in oil, will closely resemble the chrome greens. It is therefore of the greatest importance to obtain the most suitable shade of zinc yellow for making the best zinc greens; but unfortunately this is not such a simple matter as it may appear at first sight. The purity of the zinc oxide for producing the yellow is undoubtedly of the utmost importance; and next to this is the temperature at which the zinc chromate was made. With regard to the most suitable zinc white, the finest brand on the market should always be used irrespective of price, namely, the so-called "snow white" (zinc white, "green seal"). The next lower grade on the market—namely, "red seal"—is not suitable for the preparation of a high quality zinc yellow, and still less suitable is the inferior black seal grade of zinc white.

The temperature used in making zinc white must not be below 50° C., or much above this limit. In either case the resulting zinc yellow is very coarse-grained and decidedly reddish in tone—faults which are transmitted to the greens produced from it.

The Zinc yellow is formed in the following way: The zinc white, finely distributed in water, is treated with a certain quantity of concentrated sulphuric acid and thereby partly converted into zinc sulphate, which is afterwards precipitated with a concentrated solution of potassium bichromate. The resulting product consists essentially of a double salt, zinc orthochromate and potassium bichromate, $3(ZnCrO_4)K_2Cr_2O_7$, besides variable quantities of zinc oxide. This latter certainly exists unchanged, and it seems impossible to obtain the right compound and its characteristic primrose or sulphur yellow shade without it. The pigmentary substance, of course, is the compound $3\ (ZnCrO_4)K_2Cr_2O_7$, and the presence of potassium bichromate, $K_2Cr_2O_7$, explains the partial though very slight solubility of dry zinc yellow in cold water, and more particularly in hot water. The sodium chromate often used in place of the somewhat expensive potash salt being unable to form such double salts, it cannot be employed for making zinc yellows of the above composition.

In making zinc chrome on the large scale, the zinc white used must be first specially treated to prevent the formation of a granular yellow, which may easily occur under careless management, especially if the zinc white has not been distributed sufficiently fine in the water. In the sulphuric acid treatment the coarser particles offer a stubborn resistance to the influence of this reagent. The zinc sulphate forms hard granules with the acid, and the coarseness is increased by the influence of the potassium bichromate added later on to such an extent that even the most careful grinding cannot alter the granular nature of the zinc yellow. This fault, however, will be avoided—largely, if not entirely—if the zinc white, before applying the sulphuric acid, be converted into such a uniformly disintegrated condition that the acid can act evenly on all parts of the mass For this purpose the zinc white must be sufficiently ground with water in a large cone mill (Fig. 8), the resulting impalpable paste being afterwards washed by levigation through a fine hair or silk sieve into the tank. The weighed quantity of concentrated sulphuric acid (66° Bé) is then added, the sooner the better. Since the operation, however, is invariably accompanied by a considerable rise in temperature, the whole mass must be thoroughly well stirred to ameliorate the violence of the reaction,which increases with the temperature of the liquid in the tank.

The volume of water taken for grinding and levigating the zinc white should be such that the temperature during the sulphuric acid treatment will not fall much below 50° C. With a little practice it will be easy to get the temperature right without a thermometer. After all the prescribed quantity of sulphuric acid is in, the solution of potassium bichromate must be added at once, the temperature of this solution being regulated in accordance with that of the existing contents of the tank. Should this from any cause be much below 50° C., the potassium bichromate solution must be heated so as to restore the temperature to 50° or a little higher. Conversely, if the contents of the tank be too hot they must be cooled by means of the bichromate solution. Experience shows that the best results as regards the brightness of the zinc chrome will be obtained when the potassium bichromate solution is added directly after the zinc sulphate is formed. It is necessary therefore to prevent any waste of time in the operation arising, for instance, through delay in dissolving the potassium bichromate or any other cause, since the prolonged standing of the mixture of sulphate and oxide of zinc will not only cool the mass but also produce granulation, thus jeopardising the success of the whole operation. With regard to the concentration of the bichromate solution, this is not so very important in working on a large scale as it seems to be from trials made in the laboratory. It should not be diluted to excess, though, provided the prescribed temperature be exactly maintained, comparatively weak solutions have no appreciably unfavourable influence on the appearance of the resulting zinc chrome, all that occurs being a considerable delay in the formation of the product. The solution of bichromate must be vigorously stirred in for at least half an hour afterwards.

It is an essential condition to the success of the whole operation that the zinc chrome when formed should be allowed to remain undisturbed at least 12–16 hours, since it is only after the lapse of this period that the formation of the double salt, $3(ZnCrO_4).K_2Cr_2O_7$, will be completed. As this progresses the mass continues to shrink, and the better the precipitate settles down to the bottom. Nevertheless, if the process runs a normal course the precipitate will be considerably more voluminous than is the case with most of the other yellow mineral colours. The clear liquid gradually separating above the precipitate always contains a larger or smaller quantity of surplus bichromate; and this seems essential to the formation of a bright zinc chrome, and consequently—since this quality naturally depends upon the content of zinc orthochromate—to the formation of the latter in sufficient quantity as well, for so soon as an attempt is made to prevent this surplus by reducing the prescribed quantity of bichromate the resulting product bears not the slightest resemblance, especially in the dry state, to the real zinc chrome.

The supernatant liquid, charged with bichromate, is next separated from the precipitated zinc yellow by decantation and poured into a special tank large enough to hold the liquor from 3–4 batches of zinc chrome. This tank being filled about three-fourths full with the said liquor, the contained bichromate is precipitated by thorough stirring with a dilute cold solution of sugar of lead, the resulting precipitate when thoroughly washed with cold pure water furnishing a very useful, chemically pure chrome yellow (*q.v.*) as a by-product.

The zinc chrome remaining in the working tank must next be washed at least twice with cold water. The washings, although always containing bichromate, are useless, and are run off into the drains without any further consideration, since it would not be profitable to use them for manufacturing chrome yellow in the above described manner, owing to the very small yield obtainable.

Although in washing out the zinc chrome it is very likely that a portion of the potassium bichromate in the compound, $3(ZnCrO_4).K_2Cr_2O_7+xZnO$, dissolves and is lost in the washings, this washing is by no means superfluous, since imperfectly washed zinc chrome has many defects in comparison with the really pure article. Thus it will always have a reddish tinge, which, however unimportant it may seem beforehand, will be very much in evidence in the shade of the green obtained by mixing the yellow with blue. Moreover, the pigment is much harder and denser when dry, and is therefore very difficult to work up into green, and the product is deficient in covering power in comparison with those produced from zinc chrome that has been washed properly.

After washing, the zinc chromate is filtered in the ordinary manner, pressed, cut into lumps, and dried in drying chambers or in the open air.

Although from the natnre and properties of the compound there can be only one really useful kind of bright zinc chrome, the proportions of the raw materials used by different makers vary considerably. According to the author's experience, the most beautiful shade and the highest yield will be obtained from the following proportions:

Zinc white, green seal . .	by weight	10	parts
Sulphuric acid, 66° B. . .	„	4·6	„
Potassium bichromate . .	„	10	„
	Yield	18·9	zinc chrome.

Any reduction, though only a small one, in the weight of one or other ingredient immediately affects the result, and always gives an inferior product.

The described process was devised in 1847 by Murdoch, who abandoned the older methods employing zinc chloride or zinc sulphate, which salts are more or less unsuitable because they must always be freed beforehand from the iron invariably present. Moreover, the precipitates obtained by precipitating zinc salts with bichromates or chromates are extremely unstable. When they have been thoroughly washed only about 40 per cent. of the calculated yield is obtained, and if they are not washed the produce, though good in shade, will be very hard and granular and quite useless as a pigment.

In the drying process zinc chrome is very stable, the shade being unaffected by either very high or very low temperatures. It is perfectly fast to sulphureous gases, and may be mixed with any colours containing sulphide sulphur.

As zinc chrome is not washed very carefully, it may of course under certain circumstances contain traces of acids or salts, capable of injuring the pigment when ground in oil.

All inorganic and many organic acids, as also ammonia and an excess of caustic alkali, will dissolve zinc chrome. Any undissolved residue indicates adulteration, in which connection chrome yellow is chiefly concerned. When treated with ammonium sulphide or sulphuretted hydrogen, zinc chrome should not turn brown or black. The quantitative ultimate analysis of zinc chrome never gives concordant results, so that the chemical composition has not yet been ascertained. This very interesting colour is supposed to consist of basic zinc chromates or acid potassium-zinc chromates.

2. Chrome Yellow (*Chromes, Chromgelb, Jaune de Chrome*)

The so-called chrome yellows are not only of the highest technical importance among the yellow colours, but must also be considered individually as the most important of the mineral colours. In addition to their excellent technical qualities, their scale of gradation is not even approximately equalled by other mineral colours. The shades of the chromes comprise all imaginable gradations from the lightest sulphur yellow to the darkest (reddish) orange, and from this to the richest deep violet red—a range which cannot be surpassed. At the same time it is a fact of special importance to the manufacturer that each member of the chrome yellow group can not only be obtained by mechanical mixtures of light and dark shades, as is mostly the case with the green colours, for instance, but each member can also be produced independently according to distinct and entirely different formulæ.

The light chrome yellows, when perfectly pure, consist, notwithstanding differences of shade, to a certain degree of neutral chromate of lead, $PbCrO_4$, only. In proportion, however, as the shade gradually passes into reddish orange it may be assumed with certainty that more and more of the neutral lead chromate has been converted into the basic compound, so that the chrome yellows which are redder than the lemon chrome, without belonging to the real orange chrome, must be regarded as mixtures of more or less neutral and basic lead chromates. This opinion seems to be the more correct inasmuch as the same shades can be produced (though with less brightness) by mechanically mixing dry neutral lead chromates (pale chrome) with basic lead chromates (orange chrome). The circumstance that the pale chrome yellows of identical chemical composition differ widely in shade is due to the different molecular condition of the lead chromates. This condition seems to depend mainly on the temperature to which the lead chromates are accidentally or designedly exposed during or after formation. The more the neutral chrome yellows pass over into the basic modification, the more will the crystalline form predominate in the resulting compound, the yellow then becoming darker and redder, and also specifically heavier, inferior in covering power when ground in oil, and considerably looser in the dry state, so that the cones or lumps formed from the wet mass have very little durability in the dried state. Perfectly pure basic lead chromate, the most important representative of which is the technical red chrome, should accordingly exhibit the most decidedly crystalline form, which is actually the case. Hence, to produce a certain shade of chrome yellow in exact accordance with distinct calculations, it is primarily important that it should acquire the molecular form peculiar to the lead chromate in question.

As with all crystalline bodies highly concentrated solutions favour the rapid formation of crystals, so by using insufficient quantities of water in the manufacture of chrome yellows, crystalline, dark colours alone are always obtained. Conversely, lighter and more brilliant chrome yellows will be obtained in proportion as the quantity of water used for precipitation is increased; and the production of every individual member of the long scale of colours of the chrome series must depend in all cases on the use of a definite quantity of water. Practical experience shows that this deduction is in full harmony with facts, the maintenance of accurately defined quantities of water being one of the most important factors for obtaining a predetermined shade of colour.

The accuracy of this first rule to be followed in the manufacture of perfect chrome yellows can be easily checked by the following parallel experiments. When in producing two chrome yellows according to the same formula twice the quantity of water is taken in the one case as in the other—the treatment being exactly the same in other respects—it will be found without difficulty that a considerable difference in appearance exists between the dried products. The yellow made with the larger quantity of water will be considerably lighter in shade than that made with half the quantity of water.

The continued stirring of the solution is well known to influence the formation of crystals, so that instead of the large and perfect crystals obtained when the liquid is left perfectly quiet the resulting crystals will be in a finely divided form (needles or splinters), of the type known in commerce as crystal powder. By stirring the liquors during the process of crystallisation the perfect formation of crystals will be retarded, a fact which, when applied in the manufacture of chrome yellows, will have a very important influence on their appearance; for, since the precipitation of lead chromate takes place, as already mentioned, from very dilute solutions of the raw materials, the continued stirring of the mass before and after the formation of the precipitate will furnish a product which is paler and brighter than that obtained with the formula described above, but at the same time softer and specifically lighter. This striking phenomenon can be explained without difficulty by aid of the foregoing hypothesis. On account of the continued active stirring of the liquid, the transition of the lead chromate into the crystalline form will be successfully prevented. In such case the chromate will be transformed into an extremely fine state of division, or at least the condensation of the chrome yellow will be prevented when the precipitate has been deposited from such highly dilute solutions that any higher degree of fineness would be impossible. The finer, however, the texture of the chrome yellow, the brighter, softer, and specifically lighter it will be when dry.

Even though the foregoing conditions with regard to the use of a uniform quantity of water and continued stirring during the precipitation of the lead chromate be observed, the resulting products are liable to vary unless three other important factors be considered at the same time, namely: (1) The temperature at which the lead chromates are formed; (2) the time consumed in this operation; and (3) the method of washing the colour after precipitation.

With regard to suitable temperature, the general rule is that the shades are lighter in proportion as the temperature is lower, and, conversely, have a more reddish tinge in proportion as higher temperatures are employed. Rising temperature seems, therefore, to accelerate the crystallising of the precipitated lead chromate, the same result being obtained by treating the finished dry pale chrome yellow with boiling water. Of course, the variation from the original shade is not so striking as it would be on direct precipitation in the hot state. Besides having a much more reddish tinge, the resulting yellow differs essentially in other respects from the chrome yellows obtained by cold precipitation. The otherwise finely divided precipitate is flaky when a higher temperature is used, and, on settling down, forms a very voluminous spongy mass, which filters very quickly, and shrinks considerably under pressure, parting with a large quantity of water. The resulting lumps of dry colour exhibit a peculiar fibrous or felted fracture, and have an unusually low specific gravity.

The same changes occur in the pale chrome yellows when the manufacturing processes, especially the washing, take an unusually long time to carry out. Even when the washing is performed as rapidly as possible there is an appreciable darkening of the colour, and this change is naturally intensified by prolonging the washing process. This very important circumstance must be borne in mind when making the lemon chromes, as well as the very pale grades. Moreover, when all the conditions for producing a perfect chrome yellow have been fulfilled one can never preserve the initial shade of colour through the whole series of operations. Hence when any brand of chrome yellow is being matched allowance must always be made for the unavoidable darkening of the lead chromate in the washing process; and the margin will be greater in proportion as the desired shade of chrome yellow is paler. Consequently it is quite impossible to obtain the very palest brand of chrome yellow by the usual simple method of precipitation. In fact, as will be seen further on, special measures must be taken to prevent the subsequent darkening of these grades in the indispensable process of washing the lead chromates. By summarising the foregoing observations we arrive at the following rules, which must be observed strictly in the manufacture of all chromes except the orange grades:

(*a*) Use a maximum of water and very dilute solutions.

(*b*) Stir thoroughly and continuously during and after the formation of the chrome.

(*c*) Maintain the lowest temperatures possible.

(*d*) Avoid any loss of time both in the forming and, more especially, the washing process.

The use of perfectly pure raw materials is, of course, a *sine quâ non.*

In the course of time, and with the advance of technical knowledge, all the soluble and most of the insoluble lead salts have been used to manufacture the different shades of lead chromes, the result being the gradual accumulation of a great number of formulæ, each giving a different product, according to the raw material used. Nevertheless, the only chrome salts now used for precipitation are potassium chromate and (more recently) sodium chromate, which is somewhat cheaper, both the acid and the neutral salts being employed. The first-named is met with in commerce in the form of the bichromate only, and the neutral compound has to be prepared by neutralising this with soda, whereas sodium chromate can be obtained both as acid and neutral salt.

For making chrome yellow the most important of all soluble lead salts is *neutral lead acetate—the sugar of lead* already mentioned in the manufacture of white lead—though lead nitrate and the sparingly soluble lead chloride are both now largely used. Of the insoluble lead compounds, white lead has become very important for the manufacture of chrome yellows, and also lead sulphate to a smaller extent.

Lead acetate is only met with in commerce as the crystalline sugar of lead; it is either used direct (this being the more general way), or for making basic lead acetate or to manufacture basic lead chromates, and serves then as a raw material. This latter is made by boiling a solution of sugar of lead with finely ground litharge until no more litharge is dissolved. This operation, however, has been already described in the manufacture of white lead by the French process (*q.v.*).

The size of the crystals of sugar of lead for manufacturing chrome yellow is immaterial; the sole essential point is to take a pure, colourless article, the brown sugar of lead, produced from pyroligneous acid, being unsuitable for the majority of chrome yellows. Sugar of lead crystallises in four-sided prisms, readily soluble in water, and melting at a moderate temperature. It has the chemical formula $Pb(C_2H_3O_2)_2.3H_2O$.

Lead nitrate, $Pb(NO_3)_2$, exists in commerce in the form of a heavy salt, forming large milk-white octahedral crystals, readily soluble in water. It is prepared by dissolving lead oxide or metallic lead in dilute nitric acid.

Lead chloride, $PbCl_2$, forms in the crystalline state small white, brilliant needles and hexagonal plates, but also occurs as a heavy, soft, white powder. In either case it is very difficult to dissolve in water. This compound is most easily obtained by treating lead oxide with hydrochloric acid, or by mixing a soluble salt of lead with a solution of common salt or hydrochloric acid, whereupon it is precipitated as a dense white crystalline body. Low-price cost of production having to be considered in the application of lead chloride for manufacturing chrome yellow, it is advisable to decompose commercial white lead with hydrochloric acid. For this purpose powdered white lead, ground very fine with water on a cone mill, as described in the use of white lead for making zinc yellow, is treated with pure commercial hydrochloric acid until effervescence (liberation of carbon dioxide) ceases, care being taken to avoid any considerable excess of the acid. Should this, however, occur it can be neutralised by adding white lead in small quantities, thoroughly stirred in, so long as effervescence continues. The resulting lead chloride is in an extremely fine state of division, and can be used direct for making lead chromate, since it forms chrome yellow on treatment with neutral potassium or sodium chromate. Lead chloride, or at least the basic modification $PbCl_2.Pb(OH)_2$, can be obtained still more cheaply by treating finely ground litharge for several days with a concentrated solution of common salt, and stirring up the pasty mass at intervals. The best plan is as follows: 100 parts of finely ground litharge are mixed in the dry state with 10 parts of common salt, and this mixture is placed in a large cast-iron pan, or staunch wooden vat, with enough warm water to form a fairly stiff paste. After about twelve to fifteen hours, during which time the mixture has frothed up considerably, it must be thoroughly well stirred. When the consistency has so increased that the mass can no longer be easily stirred, it must be diluted again to the original strength with warm water, and this operation repeated at intervals of twelve to fifteen hours, until all the lead oxide has been decomposed, *i.e.*, until the reddish shade of the mixture has given place to white, whereupon the conversion of the litharge into lead chloride may be considered as complete. With a temperature of 20 to 24° C. this will be generally the case in four to five days, or proportionately earlier at higher temperatures. In this reaction the lead oxide abstracts chlorine from the common salt and combines with it to form lead chloride, $PbCl_2$, which, on account of its affinity for lead oxide, combines with another portion of that substance and the water present, caustic soda being formed as a by-product:

$$\underbrace{2PbO}_{\text{Litharge}} + \underbrace{2NaCl}_{\text{Common salt}} + \underbrace{2H_2O}_{\text{Water}} = \underbrace{PbCl_2.Pb(OH)_2}_{\text{Basic lead chloride}} + \underbrace{2NaOH}_{\text{Caustic soda.}}$$

The presence of caustic soda is a drawback to the employment of the mixture in manufacturing light shades of lead chrome, and for this purpose the alkali must be removed by washing with cold water, or by neutralisation with a mineral acid. The direct application of lead chloride containing caustic soda is only feasible in producing basic chrome yellows (orange chrome, red chrome), which are gradually formed on the addition of a concentrated solution of potassium bichromate, though the neutral chromate acts immediately.

Of the insoluble lead combinations, white lead is the principal one coming under consideration. Treated with neutral potassium chromate, it is completely transformed into basic lead chromate; this reaction forms the basis of the manufacture of red chrome. When used for making chrome yellow, the white lead must not only be ground in a dry state, but also repeatedly ground extremely fine in a wet state, which can be effected in a large funnel mill when no wet mill is available. It seems as though bright and really brilliant chrome yellows can only be produced with brands of white lead containing the normal proportion of lead hydroxide, since the decomposition of potassium chromate with French white lead, for instance, is very imperfect, at least according to the ordinary formulæ for making pale chrome yellows, and especially by the cold process. The resulting lead chromates have a faded look, and are very heavy when dry, in comparison with those obtained under the same conditions from German white lead. The actual degree of whiteness of the white lead used seems, however, to have only a very slight influence, if any, on the brightness of the resulting chrome yellow.

The application of lead sulphate in the manufacture of chrome yellow, for certain kinds of which it is very useful, has become rare. When used indirectly, *i.e.*, precipitated from sugar of lead by sulphuric acid, in presence of any suitable lead chromate, it still plays a very important part in the manufacture of the canary yellow brands of chrome. The precipitation of such lead chromates is effected as follows: Potassium chromate is treated with a certain quantity of sulphuric acid, and the mixture employed to precipitate a suitable quantity of sugar of lead solution According to the quantity of lead sulphate thus precipitated, the resulting chrome yellows will become paler, and do not darken in shade, or only a little, in the washing process. Instead of sulphuric acid, sulphates, such as alum, aluminium sulphate, Glauber salt, &c., may be mixed with the bichromate, since, like sulphuric acid, they have the property of forming lead sulphate with sugar of lead. It appears, however, that the resulting lead sulphate has somewhat different properties from that precipitated with sulphuric acid and sugar of lead, since the chrome yellows obtained in this way (especially the very pale brands) settle down only very slowly on washing, and the wash waters always contain a certain quantity of lead sulphate and lead chromate in a finely divided state, producing an opaque, milky appearance. This is not removed by passing the washing through filtering paper, the precipitate of lead sulphate being so fine that it will traverse the pores of the best paper.

Potassium Bichromate, $K_2Cr_2O_7$

In describing the manufacture of zinc yellow we had an opportunity of dealing with potassium bichromate, which is one of the most important salts used not only in the preparation of mineral colours, but also for technical purposes in general. With regard to the most important and versatile part played by this salt in the manufacture of lead chromates, it is advisable to go thoroughly into the description of the manufacture and properties, &c., of this bichromate. To properly and correctly understand the whole process of making chrome yellow it is essential to have a correct knowledge of the functions of this chromium compound in the successive chemical reactions with soluble and insoluble lead salts.

Potassium bichromate (acid chromate of potash) is manufactured indirectly from chrome ironstone, the richest chrome mineral existing in nature. The chrome ironstone has the chemical formula $FeCr_2O_4 = FeO.Cr_2O_3$, and consists essentially of ferrous oxide and chromic oxide. The chemical processes for effecting the recovery of the valuable chromic oxide from chrome ironstone are based entirely on the oxidation of the chromic oxide to chromic acid and of the ferrous oxide to ferric oxide. Potassium nitrate (saltpetre) was formerly used as the oxidising agent. By the calcination of this substance with finely crushed chromic ironstone the chromic oxide is oxidised to chromic acid. This latter combines with the alkali, first of all to form potassium chromate, from which the acid potassium chromate is afterwards obtained by acidification with sulphuric or nitric acid. Since in using the saltpetre by itself the oxygen only is able to react, so that the cost of the operation is needlessly enhanced, this part is replaced in practice by an equivalent quantity of another potassium salt (potash, potassium carbonate, K_2CO_3), that is also capable of forming soluble chromates with chromic acid. Boiling water dissolves the resulting potassium monochromate out of the ground fused product, together with undecomposed potash and the soluble potassium aluminate and silicate. After the alumina and silica have been precipitated by adding wood vinegar, this solution of chromate is evaporated until a skin begins to form on the surface of the liquor, a sign of incipient crystallisation of the potassium monochromate. When left undisturbed, the latter will crystallise out in lemon coloured rhombic prisms. The resulting potassium monochromate is readily soluble in water, and evinces a strong tendency to change gradually into potassium bichromate.

The conversion of the monochromate into bichromate is based on the circumstance that some acids are able to abstract from the former nearly one-half its content of potassium, forming salts which are readily soluble and therefore easily separated from the sparingly soluble potassium bichromate, by a simple process of crystallisation. On account of its very low price, sulphuric acid especially is used for this purpose, nitric acid being also used for, certain reasons that will be explained later on. The weighed quantity of monochromate is treated with about one-fourth of its weight of sulphuric acid, and the formation of the two above-mentioned acid salts takes place at once. For instance, if 80 parts of potassium monochromate are dissolved in 160 parts of water and treated with 20 parts of concentrated sulphuric acid, the whole being gradually raised to the boiling-point and left to stand, the red potassium bichromate crystallises, whilst the acid potassium sulphate remains dissolved. If less sulphuric acid, say one-eighth of the weight of monochromate, were used, there would be formed, in addition to the potassium bichromate, the normal potassium sulphate, which is very difficult to separate from the mixture, owing to the very little difference in the solubility of the two salts at all temperatures.

The chemical reaction in the decomposition of potassium monochromate with nitric acid is on exactly the same lines as with sulphuric acid. In addition to the bichromate potassium nitrate is formed, and this can be recovered and used afresh for producing the monochromate from chrome ironstone. For this reason the process will be more advantageous than the sulphuric acid method, since in the latter the bulk of the potassium sulphate is lost or expensive to recover.

The process used at present dispenses with the expensive potassium nitrate for preparing the monochromate. The finely crushed chrome ironstone is mixed with lime and potash, and the mixture roasted in a reverberatory furnace, the charge being frequently turned. The greenish-yellow roasted product, consisting mostly of potassium chromate, calcium chromate, and ferric oxide, is bleached with water, the two first-named salts passing into solution, and leaving the insoluble ferric oxide at the bottom of the tank. The solution of chromate, separated from the ferric oxide, is treated with a solution of potash (potassium carbonate), which throws down calcium carbonate and transforms the calcium monochromate into potassium monochromate. The solution of potassium monochromate is separated from the precipitate and treated further with sulphuric or nitric acid, so as to convert it into potassium bichromate, as described above. The potassium bichromate obtained in this way forms red, triclinic crystals, and is readily soluble in hot water, but very sparingly so in cold water (10 : 100 at 15° C.). Under gentle heat the crystals readily melt, but without alteration, but stronger calcination decomposes them into neutral potassium chromate, chromic oxide, and oxygen. The solution of the bichromate has an acid reaction, a bitter metallic taste, and is easily reduced by organic substances. Whereas in the cold the solution remains a long time unchanged when treated with sulphuric acid, the same acid added to a hot saturated solution will precipitate chromic anhydride. When heated, this solution readily disengages oxygen and decomposes into a mixture of chromic sulphate and potasssium sulphate, from which crystals of chrome alum, $K_2Cr_2(SO_4)_4 + 12H_2O$, separate after some time. Potassium bichromate being the only potassium chromate in commerce, the monochromate being very rarely met with in the market, is the only one used in the manufacture of most of the other chromates.

Nowadays sodium chromate is also manufactured. Although this salt is cheaper, since calcined soda can be used instead of potash, the roasting process being similar in both cases, it is not very largely used in the manufacture of chrome yellow, probably because sodium bichromate is very deliquescent, and therefore difficult to store and estimate, whilst at the same time the larger quantity required to furnish the same result tends to equalise the difference in price as compared with potassium bichromate.

a. Manufacture of the Sulphur-yellow (Canary) and Pale Lemon Chromes

In laying down the general rules to be observed in the manufacture of the paler coloured chromes reference was made to the fact that the precipitation of potassium bichromate with soluble lead salts will not furnish the very light shades, viz., the sulphur- (or canary-) yellow brands of the chrome yellow, because the precipitate darkens in the indispensable washing process so considerably that the product must be classed as dark lemon chrome when dry. It is quite another thing, however, if a certain quantity of lead sulphate be formed with the lead chromate by adding sulphuric acid or a soluble sulphate to the solution of potassium bichromate, and precipitating the solution of lead salt with this mixture. The chromes obtained in this way do not darken in washing, and are not liable to change so easily as the simple chromes, where this disagreeable phenomenon is quite a matter of course. This resistance of the chromes containing co-precipitated lead sulphate to influences which would overpower the other lead chromates is noticeable even when the quantity of sulphuric acid is very small in proportion to the potassium bichromate, but becomes still more pronounced as the quantity of sulphuric acid is increased. Consequently the colour of the resulting chromes is modified in the same proportion—*i.e.*, they become paler as the amount of sulphuric acid is increased, and darker, *i.e.*, more reddish, under the converse conditions.

Experience shows that really usable dry chromes can only be obtained when the proportion of sugar of lead and potassium chromate taken for the precipitation process is such that there is an excess of at least 5 per cent. (by weight) of the latter ingredient. It is true that the tendency of the chromes to darken quickly in washing cannot be altogether avoided, but they are much brighter in appearance than when neither of the salts is in excess. In view of this not more than 37½ parts of potassium bichromate should be used in practice to each 100 parts of sugar of lead; and this proportion will apply to nearly every case.

Consequently when a certain addition of sulphuric acid is used in producing sulphur-yellow chromes, the proportion between sugar of lead and potassium bichromate must be altered so that the said excess of 5 per cent. of the first ingredient is still maintained in relation to the sum of the other raw materials, and in order to ensure this when an increased quantity of sulphuric acid is taken the quantity of bichromate must be decreased in due proportion. This proportion is expressed in figures as follows: $0{\cdot}65\ H_2SO_4 : 1{\cdot}00\ K_2Cr_2O_7$; or, practically, when the quantity of sulphuric acid is increased by 0·65 the quantity of bichromate must be reduced by 1·00 part (by weight) to maintain the normal proportion between sugar of lead and potassium bichromate, corresponding to an excess of about 5 per cent. sugar of lead in the precipitation process. This is clearly shown in the following Table:

Brand.	Sugar of Lead.	Sulphuric Acid, 66° Bé.	Potassium Bichromate.	Brand.	Sugar of Lead.	Sulphuric Acid, 66° Bé.	Potassium Bichromate.
No. 20	100	—	37·5	No. 10	100	6·50	27·5
,, 19	100	0·65	36·5	,, 9	100	7·15	26·5
,, 18	100	1·3	35·5	,, 8	100	7·80	25·5
,, 17	100	1·95	34·5	,, 7	100	8·45	24·5
,, 16	100	2·6	33·5	,, 6	100	9·10	23·5
,, 15	100	3·25	32·5	,, 5	100	9·75	22·5
,, 14	100	3·90	31·5	,, 4	100	10·40	21·5
,, 13	100	4·55	30·5	,, 3	100	11·05	20·5
,, 12	100	5·20	29·5	,, 2	100	11·70	19·5
,, 11	100	5·85	28·5	,, 1	100	12·35	18·5

In this table No. 1 represents the lightest, No. 20 the darkest shade of chrome of this series, all the intermediate numbers representing so many different shades. The brands 1–10 may be termed for trade purposes sulphur yellow, and 11–19 pale lemon. A still further subdivision of shades can, of course, be obtained by varying the quantity of sulphuric acid, for instance, by only 0·325 part by weight and the bichromate by 0·5 part respectively. Other modifications are possible, provided the ratio 0·65 : 1·00 between the sulphuric acid and bichromate be invariably maintained. How this can be done will be seen by the following example, in which the weight of sulphuric acid is increased by 0·5 part, the equation being:

$$0·65 : 1·00 = 0·5 : x;$$

i.e.,

$$x = \frac{0·5}{·65} = 0·77.$$

$$\left[\text{Orig. has } = \frac{10·5}{65} = 0·77\right]$$

This means that the weight of potassium bichromate must here be reduced to 0·77 part. The use of basic lead acetate for producing the sulphur chromes will not alter either the process or the result. On the other hand, it must be borne in mind that the most advantageous basic lead acetate to use is one containing exactly double the quantity of lead oxide in proportion to the acetic acid present, as is the case in crystallised sugar of lead. Now the latter substance, $Pb(C_2H_3O_2)_2.3H_2O$, contains in 100 parts

Acetic acid	26·92
Lead oxide	58·83
Water of crystallisation . . .	14·25
	100·00

Hence, to produce the said basic lead acetate 100 parts of crystallised sugar of lead must be treated at boiling temperature with 59 parts of litharge, the mixture being kept stirred until the litharge is completely dissolved. The resulting quantity of basic lead acetate contains as much lead as corresponds to double the quantity of sugar of lead used—*i.e.*, to 200 parts by weight.

To work with the proportions of weight given in the table, the 100 parts of sugar of lead must be replaced by 50 parts of the same and 29·5 parts of litharge, whilst the quantities of sulphuric acid and potassium bichromate remain unchanged in order to furnish the same results. This method of working may be recommended, since the cost of the resulting chrome is much less than when pure sugar of lead alone is used. The following simple calculation will clearly explain the difference in cost:

	£	*s.*	*d.*
100 lbs. crystallised white sugar of lead cost, say .	1	5	0
59 lbs. ground litharge (at 14s. per 100 lbs.) .		8	3
100 + 59 = 200 lbs. of sugar of lead will cost .	£1	13	3

So that 100 lbs. of sugar of lead will cost 16s. 8d. instead of 25s.

To manufacture pale lemon chromes at least three tanks of different dimensions are necessary. The working or precipitation tank must be as large as possible, in accordance with the rule that lead chromates are brighter and specifically lighter the larger the amount of water used in the process. If possible, the tank should be made of strong pine, measuring at least 5 ft. diameter inside and about 6 ft. high inside; but even larger sizes may be used. A smaller tank, about 3 ft. in diameter and 3 ft 6 in. high, of the same material, is used for dissolving the sugar of lead or basic lead acetate, and must be provided in the latter case with a pipe for direct steam. The third vat, for dissolving the potassium bichromate and the sulphuric acid treatment, may have the same dimensions as the last described, but can be somewhat smaller. If the tanks can be arranged as shown in Fig. 6, so much the better, especially for pale chromes; if not they may be arranged in the following manner: The precipating tank must be mounted so that the contents of the adjacent smaller vat can be gradually and conveniently transferred to the precipitating tank, one man filling the liquids into a pail, tub, or bucket, and handing them to a second, who empties them into the precipitating tank, whilst a third looks after the stirring of the liquids in the absence of any mechanical devices for that purpose.

In beginning work the weighed raw materials are dissolved, by stirring, in the smaller tank, enough water being used to ensure complete solution. This done, the tank containing the lead acetate is filled with cold water up to the top, but the bichromate tank must not be filled (with cold water) more than three-fourths full. The former is left to stand, after efficient stirring, in order that any impurities may settle down, the weighed quantity of sulphuric acid is thoroughly stirred in with the solution of bichromate, and the tank then filled up to the top, the mixture being afterwards allowed to stand for some time.

Meanwhile the precipitating tank is filled about half full with pure cold water, and to this is added the clarified solution of lead acetate—run in through a fine hair or silk sieve—the whole being constantly stirred to mix the water and lead acetate intimately together. Next follows the mixture of bichromate and sulphuric acid, in a very thin stream, in order to produce the lead chromate in the finest possible state of division, stirring being continued without any interruption during the precipitation and for half an hour afterwards. The method of adding the solution of bichromate is of the highest importance to the quality of the resulting chromes, it being essential to run the solution in as an extremely attenuated stream, regularly and without cessation. This being very difficult to secure by hand, the work must be entrusted to a thoroughly experienced and conscientious man. Of course it will be still better to perform the whole operation by means of the arrangement shown in Fig. 6.

When the precipitate of lead chromate has settled down sufficiently in the tank—which usually does not take long—the top liquid, which must be always quite clear and colourless, is drawn off as completely as possible.

The next process, that of washing the chrome, must be performed very carefully and without any loss of time. According as a larger or smaller working tank is used, the washing must be repeated twice or three times. In many works it is the practice to add 1¼ to 1½ lbs. of sugar of lead to the washing waters, a precaution that is very commendable. Finally, the washed precipitate must be filtered as quickly as possible, pressed, and the resulting paste moulded into square or round lumps, or into cones. It must be dried out of doors, or at 35–50° C. in artificially heated drying-rooms. The "sharp"—*i.e.*, quick—drying, recommended by many authors, is very injurious to the pale chromes, and must therefore be condemned.

The most contradictory opinions exist about the chemical functions discharged by the co-precipitated lead sulphate in these chromes. It is believed by some that these chromes should be considered as double compounds, lead sulphochromates; but, on the other hand, the possibility of such compounds being formed is disputed. Although various circumstances seem to favour the existence of lead sulphochromates, there are also very reasonable grounds for the supposition that in this case we have only to do with a purely mechanical mixture of lead chromate and lead sulphate. The first hypothesis is favoured by the fact that the chromes obtained by the co-precipitation of lead sulphate behave quite differently, especially in the washing process, from those produced under the same conditions by precipitating the corresponding quantity of lead chromate or lead sulphate that has been formed by precipitating sugar of lead with sulphuric acid and then washed. Whilst the former chromes remain unchanged on washing, the latter darken afterwards exactly in the same proportion as the other precipitated chromes. It might be asserted that if the lead sulphate can be considered simply as an additional body in the chromes, other and similar inert bodies—*e.g.*, barytes, and, still more, blanc fixe—must give the same shades at least with lead chromate as those obtained in the former case. This, however, is not correct. The chromes produced with barytes or blanc fixe, under the same conditions, are by no means equal to the lead sulphochromates, after drying, in appearance, and in spite of the much lower specific gravity of the barium sulphate in comparison with lead sulphate ($BaSO_4$, sp. gr. 4·48–4·53; $PbSO_4$, sp. gr. 6·2–6·38) these chromes are not so light and voluminous. The latter fact is at all events very striking, and would in itself justify the supposition that the lead sulphochromates in question really exist. This, however, is apparently contradicted by the circumstance that when the sulphuric solution of bichromate is treated with a soluble lead salt, lead chromate is always precipitated first, the lead sulphate coming down afterwards. It is possible, too, to abstract the lead sulphate from the pseudo lead sulphochromate chromes by the aid of sodium hyposulphite. Though this is very difficult, it can actually be done. On the other hand, it is impossible to reconstruct a product at all similar to the original chromes by afterwards reuniting the two ingredients separated as above, even by intimately grinding them together in the wet state.

At present the manufacture of sulphur chromes from **white lead**, which is relatively much cheaper on account of its high content of lead oxide (86 per cent.), has grown considerably in favour. It is possible to prepare chrome yellow by treating white lead direct with potassium mono- or bichromate, but these chromes are of no technical value, inasmuch as their appearance is very dull and faded, apart from the heavy density of the resulting product. It is therefore necessary in the first place to convert the white lead into a soluble form. Nowadays the solvent medium almost invariably used for this purpose is nitric acid (40° B.), acetic acid being rarely employed. The general practice is to convert only part of the white lead into lead nitrate or acetate, since in the course of precipitation with potassium bichromate—alone or in conjunction with sulphuric acid or aluminium sulphate—the ready-formed soluble lead salt is attacked first, and the acid liberated therefrom by the acid precipitant gradually dissolves the unaltered white lead, until precipitation is complete. In making sulphur chrome yellows by this process it is specially important that the continuous formation of potassium nitrate or acetate by the regenerated acid and the alkali of the bichromate results in a continual decrease of the former, so that to avoid the appearance of an alkaline reaction, which would lead to the formation of a basic lead chromate, it is necessary to use at least as much nitric acid in dissolving the white lead as the complete neutralisation of the alkali in the potassium bichromate will require. This quantity of nitric acid can be easily calculated according to the equation

$$\underbrace{K_2Cr_2O_7}_{\text{Potassium bichromate}} + \underbrace{2HNO_3}_{\text{Nitric acid}} = \underbrace{2KNO_3}_{\text{Potassium nitrate}} + \underbrace{2CrO_3}_{\text{Chromic acid}} + \underbrace{H_2O}_{\text{Water}},$$

the bichromate and nitric acid being expressed by their molecular weights. The quantity of nitric acid per 100 parts of bichromate is equal to 42·71 parts of pure nitric acid (free from water).

$$295 : (2 \times 63) :: 100 : x.$$

$$x = \frac{12600}{295} = 42{\cdot}71 \text{ per cent. of pure nitric acid (free from water).}$$

But since 1 part of water-free nitric acid corresponds to 1·6 parts of acid of 40° B. strength, the above 42·71 parts must be multiplied by 1·6 * to ascertain the proportion of 40° B. nitric acid. 42·71 × 1·6 = 68·4 per cent. That is to say, in making sulphur-shaded and pale lemon chromes from white lead the amount of 40° B. nitric acid required will be at least 69 to 70 per cent. of the weight of potassium bichromate used for the precipitation in order that all the alkali present in this quantity of bichromate may be fully neutralised.

The use of aluminium sulphate instead of sulphuric acid does not cause any loss of regenerated sulphuric acid, inasmuch as the aluminium nitrate formed in the reaction with the lead nitrate acts in such a manner on the existing white lead as to form nitric acid again, together with aluminium hydroxide and carbon dioxide, the latter being liberated. The same occurs with aluminium acetate when acetic acid is used instead of nitric acid.

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* See nitric acid Table.

In other respects the treatment of these chromes is exactly the same as already described.

When **basic lead chloride** is used as the raw material for these chromes it is necessary, since this salt is always in the form of a paste, to know the percentage of water it contains before calculating the quantity required. For this purpose 20 to 25 grms. of the paste of lead chloride are weighed and dried, the result giving the dry matter in the paste. This can also be calculated from the quantity of litharge used in making the basic lead chloride, since 100 parts of litharge furnish 108 parts of dry basic lead chloride. If this quantity be taken for making, say, the No. 5 chrome yellow of our Table (see p. 138), it will be necessary to use 22·5 parts of potassium bichromate and 9·75 parts of sulphuric acid (66° B.) for the precipitation.

b. The Manufacture of Dark Lemon Chromes

If 100 parts of sugar of lead be precipitated according to the Table (p. 138) with 37·5 parts of potassium bichromate under the conditions required for the production of first-class chromes, a chrome yellow of intermediate shade between the pale and dark lemon lead chromates will be obtained. Therefore to this latter group belong all the products intermediate in shade between the above described chrome yellow and pronounced orange chrome. As already mentioned, the members of this group must be considered as a mixture of normal and basic lead chromates. The main point in their production will therefore be to obtain products consisting partly of normal and partly of basic lead chromate. The chrome yellow produced according to the above formula from 100 parts of sugar of lead and 37½ parts of potassium bichromate will be the palest representative of normal lead chromate, $PbCrO_4$, whilst the darkest is obtained by the direct precipitation of neutral lead acetate (sugar of lead) and potassium monochromate. On taking basic lead acetate instead of sugar of lead, the treatment with potassium monochromate will furnish pure basic lead chromate, *i.e.*, orange chrome (*q.v.*), but only at boiling heat. When, however, the same basic lead acetate is precipitated with potassium bichromate, a chrome yellow is obtained which must be classified with the dark lemon chromes. This indicates the method to be adopted for the manufacture of these latter, since by treating sugar of lead or basic lead acetate with a corresponding mixture of potassium bichromate and monochromate in the cold any desired shade of this series can be obtained.

The said mixture of the two chromates can best be produced by taking a solution of potassium bichromate and converting part of the salt into monochromate by neutralising with an alkali. For this purpose potassium carbonate (potash), sodium carbonate (soda) crystallised or in powder, (ammonia soda) and caustic soda may be used, but owing to considerations of price and convenience, ammonia soda is exclusively applied, so that instead of potassium monochromate the corresponding sodium salt is obtained. This, however, has no influence on the quality of the resulting lead chromate. The chemical reaction occurring in the neutralisation of potassium bichromate with calcined soda (ammonia soda) is explained by the following equation:

$$\underbrace{K_2Cr_2O_7}_{\text{Potassium bichromate}} + \underbrace{Na_2CO_3}_{\text{Calcined soda}} = \underbrace{K_2CrO_4 + Na_2CrO_4}_{\text{Mixture of sodium and potassium monochromate}} + \underbrace{CO_2}_{\text{Carbon dioxide}}.$$

From this equation it follows that for converting one molecule of $K_2Cr_2O_7$ into K_2CrO_4 only one molecule of Na_2CO_3 is required; *i.e.*, expressed in figures:

295 parts by weight of $K_2Cr_2O_7$ (molecular weight of $K_2Cr_2O_7$).
106 ,, ,, ,, Na_2CO_3 (,, ,, ,, Na_2CO_3).

(In round numbers, 30 parts of potassium bichromate to 11 parts of calcined soda.) In many works soda crystals are preferred for this purpose, the process then being naturally the same, except that units of proportion must be modified in accordance with the molecular weight of the soda crystals, viz., 286. Therefore 29 parts of soda crystals must be taken to 30 parts of potassium bichromate. The following table gives the exact proportions to be observed for the production of dark lemon chromes.

Brand or Shade No.	$Pb(C_2H_3O_2)_2$.	Basic Lead Acetate from $Pb(C_2H_3O_2)_2$ and PbO.		$K_2Cr_2O_7$.	Calcined Soda.	Soda Crystals.
1	100	50	29·5	37·5	—	—
2	100	50	29·5	37·5	1	2·7
3	100	50	29·5	37·5	2	5·4
4	100	50	29·5	37·5	3	8·1
5	100	50	29·5	37·5	4	10·8
6	100	50	29·5	37·5	5	13·5
7	100	50	29·5	37·5	5·5	14·85
8	100	50	29·5	37·5	6	16·2
9	100	50	29·5	37·5	6·5	17·55
10	100	50	29·5	37·5	7	18·9
11	100	50	29·5	37·5	7·5	20·25
12	100	50	29·5	37·5	8	21·6
13	100	50	29·5	37·5	8·5	22·9
14	100	50	29·5	37·5	9	24·3
15	100	50	29·5	37·5	9·5	25·6
16	100	50	29·5	37·5	10	27·0
17	100	50	29·5	37·5	10·5	28·35
18	100	50	29·5	37·5	11	29·7
19	100	50	29·5	37·5	11·5	31·0
20	100	50	29·5	37·5	12	32·4
21	100	50	29·5	37·5	12·5	33·75
22	100	50	29·5	37·5	13	35·10
23	100	50	29·5	37·5	13·5	36·5

No. 1 is the lightest and No. 23 the darkest shade of this group.

The formation of the chromate mixture is accompanied by the liberation of carbon dioxide, the liquid frothing up considerably. The liberation of carbon dioxide increases in violence with the quantity of soda taken. When the reaction is finished any residual carbon dioxide must be expelled from the liquid by introducing steam. The treatment of these shades of chrome, made in accordance with the above table, is exactly the same throughout as already described for the sulphur chromes.

The use of white lead, lead chloride, or basic lead chloride for making these dark lemon chromes offers no advantage, the chromes being neither brighter in shade nor more valuable in other respects than those mentioned above. Moreover, any difference in price between these raw materials and sugar of lead or basic lead acetate will be outweighed by the trouble and loss of time generally entailed by their use.

c. *Orange Chrome*

For producing orange chrome the same raw materials can generally be used as for the chrome yellows already mentioned. The composition of orange chrome, which in its purest state (chrome red) has the formula $Pb_2(OH)_2CrO_4$, indicates the desirability of using basic lead acetate for this purpose.

Neutral lead acetate (sugar of lead), as already explained, is capable of taking up a further quantity of lead oxide (PbO), and then forms (according to the quantity so taken up) basic lead acetates containing varying percentages of lead oxide. We have already become acquainted with one of these, the di-basic salt (from 100 parts of sugar of lead and 59 of litharge), of the composition $Pb(C_2H_3O_2)_2.PbO$. There is a still higher stage, the tri-basic lead acetate, of the formula $Pb(C_2H_3O_2)_2.2PbO$, which has taken up double the quantity of oxide of lead originally contained in the neutral lead acetate used for the purpose. One could also speak of a 1½ or 2½ basic lead acetate, corresponding to the formula $Pb(C_2H_3O_2)_2.\frac{1}{2}PbO$ or $Pb(C_2H_3O_2)_2.1\frac{1}{2}PbO$ respectively, the former of which could be obtained from 100 parts of sugar of lead and $59/2 = 29{\cdot}5$ of litharge, the other from 100 parts of sugar of lead and $59 + 29{\cdot}5 = 88{\cdot}5$ of litharge. If the quantity of lead oxide contained in the basic lead acetate be expressed by n, the different shades of orange chrome will be formed according to the equation

$$\underbrace{Pb(C_2H_3O_2)_2+nPbO}_{\text{Basic lead acetate containing } nPbO} + \underbrace{K_2CrO_4}_{\text{Potassium monochromate}} = \underbrace{PbCrO_4.nPbO}_{\text{Orange chrome}} + \underbrace{2KC_2H_3O_2}_{\text{Potassium acetate,}}$$

in which, as already shown, the value of n may be from 2 downwards. If $n = 1$ the resulting orange will have the formula $Pb_2(OH)_2CrO_4$; *i.e.*, it represents the highest basic lead chromate known as a pigment (see "Chrome Red"). If, however, we express n by 2, which is also permissible, an excess of lead oxide naturally results, which must be avoided, since it exerts an unfavourable influence on the brightness of the resulting orange chrome.

$$\underbrace{Pb(C_2H_3O_2)_2.2PbO}_{\text{Tri-basic lead acetate}} + \underbrace{K_2CrO_4}_{\text{Potassium monochromate}} + \underbrace{H_2O}_{\text{Water}}$$

$$\underbrace{PbCrO_4.Pb(OH)_2}_{\text{Basic lead chromate}} + \underbrace{2KC_2H_3O_2}_{\text{Potassium acetate}} + \underbrace{PbO.}_{\text{Lead oxide (excess)}}$$

To avoid this excess of lead oxide the above equation should be modified as follows:

$$\underbrace{Pb(C_2H_3O_2)_2.2PbO}_{\text{Tri-basic lead acetate}} + \underbrace{1\tfrac{1}{2}K_2CrO_4}_{1\frac{1}{2}\text{ Potassium monochromate}} + \underbrace{2H_2O}_{\text{Water}}$$

$$= \underbrace{1\tfrac{1}{2}PbCrO_4.1\tfrac{1}{2}Pb(OH)_2}_{1\frac{1}{2}\text{ Basic lead chromate}} + \underbrace{2KC_2H_3O_2}_{\text{Potassium acetate}} + \underbrace{K(OH)}_{\text{Caustic potash.}}$$

Or, more simply still:

$$\underbrace{Pb(C_2H_3O_2)_2.2Pb(OH)_2}_{\text{Di-basic lead acetate}} + \underbrace{1\tfrac{1}{2}K_2CrO_4}_{1\frac{1}{2}\text{ Potassium monochromate}}$$

$$= \underbrace{1\tfrac{1}{2}(Pb_2(OH)_2CrO_4)}_{\text{Orange chrome}} + \underbrace{2KC_2H_3O_2}_{\text{Potassium acetate}} + \underbrace{K(OH)}_{\text{Caustic potash.}}$$

The production of orange chrome according to the above formula is feasible in practice. On precipitating in the cold a striking phenomenon will be observed, viz., the formation of a slimy precipitate on adding the solution of potassium monochromate, which precipitate exhibits the characteristic pale yellow shade of normal lead chromate ($PbCrO_4$). At all events it must be considered as such, although the colour is less bright and apparently dulled by the presence of free lead hydroxide. It is only after standing for some time that the mixture gradually acquires the reddish shade of orange chrome. At the same time the precipitate loses its slimy character, shrinks considerably, and finally passes over into the crystalline form. This transformation, however, proceeds very much quicker if the precipitate be allowed to boil; and the orange chrome shade will appear at once if the raw materials are treated at boiling heat from the beginning.

The entire behaviour of the lead chromate precipitated under the above conditions leads to the opinion that in the first stage of the production of orange chrome normal lead chromate ($PbCrO_4$) is formed along with free lead hydroxide. The latter in this case acts at boiling heat exactly in the same way as caustic alkalies, *i.e.*, abstracting half the chromic acid from the chrome yellow, and thereby causing the formation of the red orange chrome (see below).

The same process also affords the possibility of producing, direct, all shades and members of the orange chrome series intermediate between dark lemon chrome and pure basic lead chromate. For this purpose, however, the value of *n* must be taken as less than unity. In this case, by using a basic lead acetate containing less lead oxide, and, consequently, more acetic acid, a loss of acetic acid will be incurred by precipitating with potassium monochromate. Hence the paler orange chromes obtained by this means cost more to produce than the darker shades, on account of the lower yield obtained.

The caustic alkalies and the alkali carbonates have the property, as already mentioned, of depriving normal lead chromate of one half its chromic acid, thereby converting it into the basic compound, orange chrome. The chemical reaction proceeds in accordance with the following equation:

$$\underbrace{2PbCrO_4}_{\text{Normal lead chromate}} + \underbrace{2NaOH}_{\text{Caustic soda}} = \underbrace{PbCrO_4.Pb(OH)_2}_{\text{Basic lead chromate}} + \underbrace{Na_2CrO_4}_{\text{Sodium monochromate.}}$$

The resulting orange chromes become more reddish in shade in proportion as the influence of the caustic alkali is more powerful and the more completely the conversion into the basic compound is effected.

The recovery and utilisation of the sodium monochromate formed in this process as a by-product is a difficult matter. On the one hand, the orange chrome tenaciously retains the dissolved monochromate, perfect separation being therefore impossible, even by repeated washing. On the other hand, the monochromate liquor is mostly of such divergent and variable composition that precipitation with basic lead acetate for the purpose of utilising the solution in the production of orange chrome invariably gives products of another shade. For these reasons the aforesaid behaviour of caustic alkalies toward normal lead chromate can only be technically applied in producing orange chrome when the resulting loss of chromic acid (in the form of sodium chromate) can be prevented.

This, however, may be done both directly and indirectly—directly by adding a corresponding quantity of caustic alkali to the sodium monochromate before precipitation; indirectly by suitable treatment of the aforesaid lead sulphochromate with caustic soda.

In the former case the process rests solely upon the use of sugar of lead, and therefore is not an advantageous one, owing to the resulting loss of acetic acid. This circumstance also explains why the method is but very little used for making orange chrome. It chiefly rests on the formation of lead hydroxide, which is precipitated along with normal lead chromate from the solution of sugar of lead by an excess of caustic soda present in the sodium monochromate, this lead hydroxide acting at high temperatures in the same way as free caustic alkalies. The process is therefore manifestly the same as when tri-basic lead acetate is taken as the raw material (see p. 144). Judging from the observed behaviour of the resulting lead chromates, it may be concluded that a means is hereby afforded for producing good orange chromes indirectly from normal lead chromates by suitably treating the latter with caustic alkalies without loss of monochromate. The means in question is the possibility of fixing the abstracted chromic acid by lead oxide. The observation, already recorded, that the formation of orange chromes from tri-basic lead acetate and sodium monochromate is accompanied by the decomposition of the first-formed normal lead chromate by the simultaneously formed lead hydroxide leads to the supposition that one half of the molecule of chromic acid in the lead chromate is more firmly combined with the lead oxide than the other half. This opinion is confirmed by the behaviour of the lead chromate in certain other respects. Bearing in mind also the well-known fact that lead sulphate is able to bind considerable quantities of chromic acid from alkaline chromate solutions, all the necessary factors are present for the conversion of the lead sulphochromates into orange chrome by suitable treatment with caustic alkalies, without incurring any loss of chromic acid. The chemical transposition herein involved is presumably as follows: The lead sulphochromate is first decomposed by the caustic alkali into basic lead chromate, lead sulphate, and alkali monochromate, the lead sulphate and the monochromate then forming more lead sulphochromate, together with free alkali sulphate, which takes no further part in the reaction. The newly formed lead sulphochromate is decomposed at once by the excess of alkali into basic lead chromate and alkali sulphate. The following equations explain these reactions:

$$(1)\quad \underbrace{2PbCrO_4.PbSO_4}_{\text{Lead sulphochromate}} + \underbrace{2NaOH}_{\text{Caustic soda}} = \underbrace{Pb_2(OH)_2CrO_4}_{\text{Basic lead chromate}}$$

$$+ \underbrace{2PbSO_4}_{\text{Lead sulphate}} + \underbrace{Na_2CrO_4}_{\text{Sodium monochromate}};$$

$$(2)\quad 2PbSO_4 + Na_2CrO_4 = \underbrace{PbCrO_4\ PbSO_4}_{\text{Lead sulphochromate}} + \underbrace{Na_2SO_4}_{\text{Sodium sulphate}};$$

$$(3)\quad \underbrace{PbCrO_4.PbSO_4}_{\text{Lead sulphochromate}} + \underbrace{2NaOH}_{\text{Caustic soda}} = \underbrace{Pb_2(OH)_2CrO_4}_{\text{Basic lead chromate}} + \underbrace{Na_2SO_4}_{\text{Sodium sulphate.}}$$

From the above equations it follows that the quantity of caustic soda to be used depends on the quantity of lead sulphate in the lead sulphochromate. Chrome yellows containing less than one molecule of lead sulphate to one molecule of lead chromate require correspondingly less caustic soda for their conversion into orange, so as to avoid a loss of chromic acid through the liberation of alkali monochromate. The resulting orange chrome will naturally be of a more yellowish shade in proportion as the percentage of lead sulphate in the lead sulphochromate was smaller. The advantage of this behaviour is evident, since it affords the possibility of manufacturing all shades, from the palest yellow to the darkest red, in the series of orange chromes separately, on the basis of exact calculations worked out beforehand. Though this process is somewhat more expensive on a manufacturing scale than the one based on the direct precipitation of basic lead acetate with potassium monochromate, the results are far more advantageous. The orange chromes obtained are not only much brighter, but also exhibit a very smooth and compact fracture and relatively high covering power—properties not always to be found in commercial orange chromes.

The practical performance of the process is unattended with difficulty, and does not require any special plant. The lead sulphochromate must first be made according to one of the formulæ given on page 137. It must be properly washed, no addition of sugar of lead to the washing waters being necessary; and the finished chrome yellow is afterwards heated to 80–90° C. The content of lead sulphate being known, the quantity of caustic potash necessary for the conversion into orange chrome can be calculated accordingly, and added at the prescribed temperature. The conversion into the basic lead chromate is visible at once, the chrome yellow acquiring a reddish tinge, which becomes more and more pronounced after continued heating, accompanied by vigorous stirring. The process may be considered as finished when no further reddening of the colour is observed on applying the contact test to a small sample. Steam is then turned off, the roduct washed two to three times with hot water, filtered, pressed, and dried. By using the Table for lead sulphochromates (page 138) the following range f orange chromes can be produced:

No.	Sugar of Lead.	Potassium Bichromate.	Sulphuric Acid (66° B.)	Solid Caustic Soda.
1 pale	100	32·5	3·25	2·7
2	100	31·5	3·90	3·12
3	100	30·5	4·55	3·64
4	100	29·5	5·20	4·16
5	100	28·5	5·85	4·7
6	100	27·5	6·50	5·2
7	100	26·5	7·15	5·72
8	100	25·5	7·8	6·24
9	100	24·5	8·45	6·8
10	100	23·5	9·10	7·3
11	100	22·5	9·75	7·8
12	100	21·5	10·40	8·32
13	100	20·5	11·05	8·84
14	100	19·5	11·70	9·4
15 dark	100	18·5	12·35	10

The preparation of orange chrome from basic lead chloride obtained as described on page 133 is both advantageous and furnishes products distinguished by special brightness of shade and low specific gravity. In the production of basic lead chloride from litharge and common salt caustic soda is obtained as a by-product, and this alkali, on the mixture being heated with potassium bichromate, effects the conversion into orange chrome, with formation of lead chromates. In proportion, now, as this free alkali is neutralised with any mineral acid, paler orange chromes will be obtained by precipitating the mixture with potassium bichromate, because in addition to the basic lead chromate a certain quantity of normal lead chromate is precipitated at the same time, this latter correspondingly shading the resulting orange chrome. The caustic soda is neutralised with hydrochloric acid or nitric acid, the former, however, being preferred on account of its lower price. The regulations which must be borne in mind in the manufacture of orange chrome from basic lead chloride are the same that apply to all the basic lead chromates, and need not be recapitulated.

d. Adjuncts mixed with Lead Chromates

The chromes are put on the market in a pure state (termed "chemically pure") as well as mixed with white adjuncts. As it is impossible to obtain sulphur and pale lemon chromes without a certain proportion of lead sulphate, it would be incorrect to exclude these chrome yellows from the former category, provided they do not contain any other adjunct. Colour manufacturers therefore put these chromes on the market as "chemically pure," and consumers accept them as such unless the content of lead sulphate in these yellows exceeds a certain limit, though, of course, the term "chemically pure" is not strictly correct. The adjuncts used by the manufacturers for the various chromes with the idea of reducing the cost of production are usually limited to barytes, gypsum, or china clay (kaolin), more rarely calcined diatomaceous earth, of which latter the lighter chromes in particular can hold a surprising quantity without the shade being affected in the least. The case is very different, however, with dark lemon chromes, and still more with the orange shades. The addition of too much white material to these chromes is rapidly detrimental, as the colour is rendered dull and pale, owing to the more crystalline character of these chromes, as compared with the sulphur-coloured chromes, not allowing of so intimate a mixture with white substances. This circumstance is specially noticeable when the chromes are finished in square or round cakes.

The practice of adding barytes to pure chromes is as general as the use of gypsum, although the lower specific gravity of the latter renders it more suitable for this purpose. True the chromes will hold twice as much barytes as gypsum to form the same strength of shade in the mixed product, but the resulting pigments are very heavy, and no cheaper, barytes costing twice as much as gypsum. An addition of china clay is advisable, especially for the very pale sulphur shades of chrome, the colour being thereby softened and acquiring a more greenish tinge. Nevertheless, the addition of china clay must not be pushed too far, since the resulting chromes are of a greasy nature, especially when in lump form.

White diatomaceous earth can only be mixed with the pure chromes in an extremely fine state of division; and even then it is used for the sole purpose of giving the colours a specially small specific gravity.

The addition of these white adjuncts to the lead chromates can be effected either in the dry or in the wet state.

In the former event the operation is preferably carried on in an edge runner mill, which undoubtedly does the work most quickly and effectually.

In most cases, however, the addition is made in a more practical manner —namely, just before or after the precipitation of the chrome. With barytes, china clay, and diatomaceous earth this will be quite immaterial. Gypsum, however, must always be added after the precipitation, since otherwise it would combine with the sugar of lead to form lead sulphate and calcium acetate.

All the materials must be diluted beforehand with water to a thin liquid mass, and in this state added through a fine silk, hair, or metal sieve to the liquid chromate in the tank, continued stirring being essential to secure intimate admixture.

Of course the mixed yellows obtained in this manner are sold at lower prices by the manufacturers in proportion to the quantity of adjunct used. They are put on the market under the names new yellow, Paris yellow, Baltimore yellow, American yellow, &c.

Chalk may be used as a diluent in dark shades of chrome only, since it has an alkaline reaction on account of its content of caustic lime. It would therefore darken light shades.

To distinguish "pure" from "ordinary" chrome yellows a sample is boiled with hydrochloric acid. Pure chrome yellow dissolves completely to a green solution, long needles of lead chloride crystallising out from the liquid when cold.

On the other hand, the presence of an insoluble residue indicates added

China clay, barytes, &c. Adjuncts—*e.g.*, gypsum—soluble in hydrochloric acid must be detected by chemical analysis.

When litharge is used as a raw material this should be tested for its content of metallic lead and copper. Metallic lead may cause very serious inconvenience to the consumer in working up the colour, whilst copper even in small quantities exerts a very considerable influence on the shade of pale chromes. The presence of acid adhering to the chrome yellow from the manufacturing process will have a most disadvantageous effect in most cases. It gives rise to considerable difficulties in grinding with oil and varnish, and acid chrome yellows (from Krems white) are specially feared by lithographic printers, since they not only fail to give a clear impression, but are also liable to corrode the sketch on the stone.

As lead colours, the chromes are sensitive to the influence of sulphur in the form of sulphides. They must not be exposed to an atmosphere containing sulphur, or be mixed with certain colours, such as ultramarine vermilion, lithopone, or cadmium yellow, all of which contain sulphide sulphur. In certain cases, therefore, these generally useful pigments must be discarded and replaced by zinc chrome.

The colouring power of chrome yellow is best determined on the basis of capacity for taking up Prussian blue—*i.e.*, its power of forming green. Of course, this test entails the use of standard comparative samples made with chrome yellow of known purity, and the same brand of Berlin blue must be used in all the tests.

3. **Naples Yellow** (*Neapelgelb, Jaune de Naples, Giallolino*)

Naples yellow is a combination of antimonic acid with lead oxide, the shade depending on the presence of a larger or smaller excess of free lead oxide. Apart from its sensitiveness to gases containing sulphide sulphur, Naples yellow may be considered a very fast colour, a condition determining its considerable use as an artist's colour. The commercial article is graded into about six shades, ranging from a peculiar pale greenish yellow to pale orange with a tendency to pink. This difference in shade is due to the different methods of production, but especially to the temperature prevailing at the time the colour is formed.

Pure acid lead antimonate (not Naples yellow, shaded by an excess of lead oxide) is obtained by treating lead nitrate with potassium or sodium antimonate for some time at boiling temperature, and calcining the resulting white precipitate after careful washing. In this state the resulting Naples yellow is at its brightest, but the process is too expensive for general employment in practice.

Another method, producing a very bright product, which is highly appreciated and used, employs potassium antimony tartrate, the well-known tartar emetic, as the raw material. The process, which is not a cheap one, relies on the decomposition of the tartaric acid in the tartar emetic by the nitric acid of lead nitrate. Antimonic acid is formed from the antimony oxide, combining with lead oxide to form lead antimonate. The application of tartar emetic for producing Naples yellow, though of only recent adoption in manufacturing practice, is an obvious method to employ, because it enables antimonic acid in its purest state to be combined with the lead oxide. The older process, however, using metallic lead as well as antimony, furnished products whose bright appearance was spoiled by the iron, arsenic, &c., accompanying these two metals. In this new process, which was first published by Brunner, 20 parts of lead nitrate and 10 parts of tartar emetic are ground to a very fine powder and mixed very intimately with 40 parts of finely crushed common salt, the resulting mixture being finally calcined for a long time in a Hessian crucible. When the mass has become liquid, after a lapse of time depending on circumstances, any further rise in temperature must be avoided. On the other hand, however, the product must be kept in a uniformly fluid state for the whole of the prescribed period. At the end of two hours it must be removed from the fire, cooled, and the hard mass washed with hot water. The colour is afterwards ground fine in water and rewashed several times. The calcined product will be brighter and harder in proportion as the temperature employed was higher, softer and more reddish under converse conditions. For this reason it is very difficult to obtain a given shade with certainty in all cases; but the process has the advantage of furnishing the best Naples yellow obtainable. Of late Naples yellow is prepared in a still more simple manner by roasting antimony oxide and pure litharge, the influence of the temperature of the roasting process being generally the same as mentioned above. The process is considered to be the cheapest at present known, and with careful manipulation enables any given shade to be produced. Amongst the older methods of producing Naples yellow the following are worthy of mention:

(1) Three parts of potassium antimonate, 12 parts of finely powdered white lead, and 1 part of ammonium chloride (sal ammoniac) are mixed together intimately, and calcined in a Hessian crucible for about an hour in accordance with the foregoing directions.

(2) Forty-nine parts of lead, 11 parts of antimony, and 3 parts of acid potassium tartrate; or

(3) Thirty-two parts of lead, 17 parts of antimony, and 3 parts of acid potassium tartrate; or

(4) Eleven parts of lead, 4 parts of antimony, and 2 parts of acid potassium tartrate are roasted together in such a manner that after fusion the metals can be oxidised by means of atmospheric oxygen, the resulting antimony oxide being then completely transformed into antimonic acid by tartaric acid. On a small scale the roasting process is preferably carried on in fireclay muffles.

(5) A pulverised alloy of 2 parts of lead and 2 parts of antimony is intimately mixed with 3 parts of saltpetre and 6 parts of common salt, and calcined in the above described manner in a Hessian crucible, the saltpetre furnishing the oxygen for oxidising the metals, whilst the common salt serves as a flux and prevents the mass from baking together. The cooled calcined product is then pulverised and washed several times with hot water.

All Naples yellows obtained by the older processes described generally exhibit the same characteristic properties. Owing, however, to their variable composition they usually differ considerably in shade owing to the fluctuating excess of one of the ingredients of the finished compound, the lead oxide, as already mentioned, being the most decisive factor influencing the shade. When the colour has been dulled by a considerable excess of lead oxide it may be brightened again by treating it with very dilute hydrochloric acid to eliminate part of the superfluous lead oxide.

Naples yellow is inferior to the chrome yellow in colouring power, but more permanent than the latter, although it may darken a little in course of time, especially when contaminated with iron, tin, or zinc. It must not be ground with iron mills or rollers.

Mixed with oil or size, it appears darker than when dry, and thus exhibits in this respect a certain similarity with glazing colours; it dries quickly, and gives pretty chamois shades. It is specially used for painting in oils, as well as on glass and porcelain. Adulteration is occasionally practised with ochre or basic lead chloride. Hydrochloric acid and nitric acid act on it only with difficulty, and furnish a colourless solution.

4. Cadmium Yellow (*Cadmiumgelb, Jaune de Cadmium*)

The different yellow pigments met with in commerce under this name are all, without exception, the same compound of the metal cadmium with sulphur, cadmium monosulphide, CdS, which differs in shade according to its physical condition. There are four to six shades of cadmium yellow, ranging from lemon to deep orange. They are all very bright, of good covering power, and therefore strong pigments; very fast to light, and by virtue of their composition almost absolutely permanent unless mixed with some other colours capable of acting chemically upon them. These qualities place the cadmium yellow in the front rank, but the very high price of metallic cadmium, which is very seldom found native, precludes the possibility of making these colours cheaply, and they are consequently very high in price. The use of cadmium yellow, therefore, like Naples yellow, is, with few exceptions, confined to artist's colours or litho and art printing, &c.

By precipitating soluble cadmium salts with sulphuretted hydrogen four modifications of cadmium sulphide can be produced, only two of which form the commercial cadmium yellow. The pure lemon modification is obtained by precipitating neutral or slightly acid soluble cadmium salts, the darker shade, resembling red lead, being produced by precipitating soluble acid salts of cadmium with sulphuretted hydrogen. Instead of the latter, which is difficult to work with in practice, the precipitation can be effected with sodium sulphide, this giving exactly the same result whichever method be used. Care must always be taken to employ cadmium salts free from zinc, otherwise the shade of the resulting cadmium sulphide will be made paler by the presence of zinc sulphide.

Unless commercial cadmium sulphate be preferred, this salt can be easily prepared by dissolving metallic cadmium in sulphuric acid. For this purpose the crushed metal ingots must be suffused with dilute sulphuric acid, in which cadmium readily dissolves, with liberation of hydrogen. The solution must be concentrated to accelerate the crystallisation of the salt. After being allowed to cool by long standing, cadmium sulphate separates in the form of large, hard, colourless crystals. When, in order to obviate the evaporation of the solution, it is used direct for the precipitation, care must be taken that it contains no excess of sulphuric acid, but is perfectly neutral. The crystals must be dissolved in water and the solution very considerably diluted with water, after which it is treated with a solution of sodium sulphide under continued stirring so long as a precipitate of yellow cadmium sulphide continues to form. This point being reached, the precipitate is allowed to settle down; the clear supernatant water is removed, and the colour washed several times with pure water in the usual manner. The precipitate is filtered, pressed, and dried. In this manner the lemon modification of cadmium sulphide is obtained.

The manufacture of the darker brands of cadmium yellow is generally effected by the dry method, cadmium carbonate being taken as the raw material. This is intimately mixed in a finely pulverised state with half its own weight of flowers of sulphur, and the mixture is then heated in a Hessian crucible. The mixture is best charged in small portions, and if the resulting yellow does not turn out bright enough the heating may be repeated, without any ill effect, in presence of a further addition of sulphur. After re-cooling the product is pulverised in the ordinary manner

Cadmium carbonate is obtained by precipitating a solution of cadmium sulphate with sodium carbonate (soda), and washing the precipitate, which must then be filtered and dried.

Sodium sulphide, used in making cadmium yellow by the wet method, can be obtained in commerce, and no advantage is gained by making it oneself. It must be always used in a fresh state of solution, the latter being very liable to decompose when kept. The reaction occurring in the precipitation of cadmium sulphate with sodium sulphide is explained by the following equation:

$$\underbrace{CdSO_4}_{\text{Cadmium sulphate}} + \underbrace{Na_2S}_{\text{Sodium sulphide}} = \underbrace{CdS}_{\text{Cadmium sulphide}} + \underbrace{Na_2SO_4}_{\text{Sodium sulphate.}}$$

The latter is eliminated by washing.

When a solution of chloride of sodium is electrolysed with cadmium electrodes, and sulphuretted hydrogen simultaneously introduced, a very intense cadmium yellow is also produced. All varieties of cadmium yellow need to be washed thoroughly. They cover well, and can be used as water or oil colours, but dry slowly. The darker shades are the more permanent ones, the lighter becoming somewhat faded in time.

Hot strong hydrochloric acid dissolves cadmium yellow to a colourless liquid. Chromes are used to adulterate this article, but furnish very unstable products. Mixtures containing white lead are to be found in commerce as *jaune brillant* (brilliant yellow).

5. Cassel Yellow (*Mineral Yellow, Veronese Yellow*)

Cassel yellow has gone out of technical use since the introduction of the far brighter chrome yellows, and is probably not to be found in commerce at all now. It can be prepared in several ways—for example, by melting together ten parts of litharge and one part of sal ammoniac (ammonium chloride). The laminated crystals of the fused product are separated from the metallic lead, and after cooling down ground with water to a very fine paste, which is pressed and dried. Basic lead chloride obtained by treating litharge with common salt also gives, when calcined in the dry state, a colour similar to Cassel yellow. This was formerly known under the name *Turner's yellow*, but has now been discarded altogether. The probable formula of Cassel yellow is $PbCl_2,7PbO$.

6. Orpiment, *or* King's Yellow

The product known under this name is arsenic tri-sulphide, with the formula As_2S_3. It is also found native, the mineral being called orpiment, or auripigment. It is obtained artificially by melting arsenic acid with sulphur, or by the distillation of a suitable mixture of pyrites and arsenical ores. As a by-product orpiment is formed in more or less considerable quantities in the roasting of arsenical pyrites in metallurgical works, on which account it has never figured as an actual product of the colour manufacturing industry. The consumption of arsenic sulphide as a pigment was already very limited before the lead chromates became known, and it is still more so now, since the arsenical colours are disappearing more and more rapidly from the market on account of their very poisonous character, so that little, if any, is still used. King's yellow may possibly be used in some cases still as an artist's colour, but, if so, it is more from habit than for its technical value; for other purposes it has become a negligible quantity. Hence it is merely as a matter of form that we now mention briefly some methods for producing orpiment. By the wet process it can be obtained: (1) By precipitating a hydrochloric solution of arsenious acid with sulphuretted hydrogen; or (2) by boiling a solution of arsenious acid in hydrochloric acid with sodium thiosulphate; or (3) by decomposing sodium sulpharsenate with dilute acid; and, finally, (4) by precipitating a solution of arsenious acid in caustic alkali with sodium sulphide.

Whilst orpiment has an orange-red shade, another compound of sulphur and arsenic—namely, realgar, AsS—is pure yellow. This compound also is found native.

7. Indian Yellow, Cobalt Yellow (*Aureolin, Jaune Indien*)

This colour too, which probably has the formula $Co(NO_2)_3 + 3KNO_2$, is only used as an artist's colour, on account of its high price. For its production an acetified solution of cobaltous nitrate is treated with a solution of potassium nitrite, the precipitate being washed, filtered, pressed, and dried. This colour is not very fast to air and light, but is unaffected by sulphuretted hydrogen.

8. Siderin Yellow (*Basic Ferric Chromate,* $Fe_2(CrO_4)_3$)

A pale orange colour of low brilliancy, and therefore only used to a limited extent as a water-colour. It is formed by heating a solution of ferric chloride with potassium bichromate. The precipitation is, however, incomplete. No special superiority as compared with other yellow mineral colours can be claimed for siderin yellow, but its property of combining with water-glass (alkali silicate) to a cement-like and extremely durable paint is valuable for certain purposes. It can be easily imitated by mixing chrome yellow with natural yellow iron pigments Siderin yellow is fast to air and light, except that it turns slightly brown.

9. Barium Yellow, Barium Chromate, $BaCrO_4$ (*Yellow Ultramarine*)

This colour, also known as *Steinbühler yellow*, is prepared by precipitating a hot solution of barium chloride with neutral sodium potassium chromate, barium yellow coming down as a sulphur-coloured precipitate. After washing it forms in the dry state a delicate sulphur-yellow powder, deficient in brightness and of insignificant covering power, and is therefore of no value as a pigment in the true sense of the word. A more important application of barium chromate is in the manufacture of matches, where it partly replaces potassium bichromate in making the igniting composition. Barium yellow is a very fast colour.

10. Tin Sulphide, SnS_2

The appearance—similar to metallic gold—of tin sulphide classes it rather with the bronzes than with the "colours," and, in fact, before the introduction of metallic bronze powders it was used exclusively to imitate gilding on wood, metal, plaster, &c. In an unpowdered state tin sulphide forms flakes or spangles of a metallic lustre and a soft golden yellow, sometimes brownish yellow, colour. Its manufacture has only been successful in the dry way, several methods, all very much alike, being used; for instance, 40 parts of finely powdered tin and 20 parts of mercury are amalgamated at a moderate heat, the resulting amalgam being crushed to a fine powder and mixed with 23 parts of flowers of sulphur and 20 parts of powdered sal ammoniac. The perfectly homogeneous mixture is next heated in a glass retort or flask (placed on a sand bath to ensure uniform heating) for about two hours, beginning at a moderate heat and raising the temperature afterwards nearly, though not quite, to red heat. It is important not to get the mass too hot, and to avoid this sal ammoniac and mercury are added, both of which vaporise below the temperature at which the tin bisulphide decomposes into the monosulphide. Iron vessels are used, too, when the manufacture is conducted on a large scale. Ammonia is liberated at first, and, later on, the mercury sublimes as vermilion, while the tin sulphide remains, partly as a sublimate on the walls of the vessel, partly as a solid mass on the bottom. After grinding in water and drying the paste, a powder is obtained, which represents the commercial form of the product. On account of its resistance to the destructive influence which sulphur exerts on metallic bronzes, it is still used for bronzing objects which are more or less exposed to dilute acids or sulphurous fumes.

Mention may also be made of:

Tungsten yellow, a deep lemon-coloured powder, obtained by grinding fine metallic tungsten powder with fused potassium carbonate. The filtrate from the lixiviated melt is precipitated with calcium chloride, whereupon calcium tungstate is formed. This must be treated again with an excess of hot dilute nitric acid.

Nickel yellow is obtained by precipitating nickel sulphate with sodium phosphate. The precipitate is pale green, turning bright yellow at a red heat. On account of its great permanence nickel yellow deserves more extensive application than it at present enjoys.

BLUE MINERAL COLOURS

In comparison with the white and yellow mineral colours described in the preceding pages the number of blue mineral colours in technical use at the present time is small. They may be divided into the following groups:

a. Blue Copper Colours

1. *Bremen blue,* consisting essentially of copper hydroxide, $Cu\ (OH)_2$, is used as a decorative colour.

2. *Lime blue,* also called *mountain blue* or *Neuwied blue,* is of very variable composition, but essentially copper hydroxide, modified by larger or smaller quantities of gypsum, chalk, lime, &c. This colour is but very seldom made or required at present.

b. Blue Iron Colours (Iron Cyanide Colours)

Prussian (Berlin) blue, in its numerous varieties and brands, such as *Paris blue, steel blue, Milori blue, mineral blue,* &c., is used in very large quantities.

c. Ultramarine Blue

The most important blue colour.

d. Blue Cobalt Colours

These groups of blue colours are so different one from another in their special properties and applications that it is impossible to discuss their general application properly without having first described the different methods of manufacture. The reader is therefore referred to the Appendix at the end of this section, where all that is worth knowing in this respect is fully discussed.

a. BLUE COPPER COLOURS

1. Bremen Blue

The consumption of Bremen blue seems to have decreased in the course of the past ten years very considerably, a circumstance that can be sufficiently explained by the introduction of artificial ultramarine and numerous blue lakes from coal-tar dyes which are at least equal to Bremen blue in point of fastness. Bremen blue is generally classed among the fugitive colours, since apart from its somewhat imperfect fastness to lime, it is very sensitive to all external influences, especially to sulphuretted hydrogen. Bremen blue is of a delicate sky-blue shade, with a greenish tinge—a shade that certainly cannot be exactly imitated by mixtures of other mineral pigments; it is probably on this account that Bremen blue has still a fairly considerable application for decorative purposes. Moreover, it has little covering power and strength, especially when mixed with adjuncts, and can only be used as a distemper colour, owing to its low covering power and liability to alteration when used with oil. For example, paints made with Bremen blue and oil turn quite green in twenty-four hours, the cupric oxide combining with the fatty acids of the oil to form a green copper soap.

A great number of methods are practised for making Bremen blue, all of them very simple in spite of pretended secrecy, and every one of them based on the precipitation of copper sulphate with caustic alkali. It will therefore be sufficient to describe only two of them, which furnish very good results. Before entering into details on this point we will first consider certain general rules, which in every case will prove very beneficial in the preparation of Bremen blue.

The chief conditions for obtaining a pure blue product are pure soft water and pure materials. If the materials, especially the copper sulphate and the water, are not free from iron, the latter will be precipitated with the copper by the caustic alkali, and the resulting yellow ferric oxide imparts to the finished blue a very disagreeable greenish shade which will be rejected by consumers; these must therefore be avoided.

The precipitation must always be performed at a low temperature (13° to 15° C., highest 20° C.), and by pouring the latter solution into the other as a thin stream, with continued stirring. The solution of alkali must not in any case be stronger than 10° B. at the most. To obtain the green precipitate containing alkali sulphate it is always desirable to keep the caustic alkali solution as dilute as possible, and effect the precipitation of the copper solution as slowly as feasible.

For toning the green precipitate blue the alkali must in no case be weaker than 28° B. or stronger than 32° B., and be absolutely cold (10° to 15° C.). In contrast to the earlier stage with the weaker alkali, the strong alkali must be added very quickly, the liquid being, of course, kept well stirred.

Great care must be taken both in the precipitation of the copper salt and in the subsequent blueing of the green precipitate that no excess of alkali is left, and, further, that as soon as the desired blue shade is obtained enough water is at hand to enable a thorough washing to be performed at once.

The finished (washed) blue is not allowed to stand a long time, if such can possibly be avoided, especially not before or during the washing process, since the brightness of the shade is very easily affected. The pale green precipitate should by no means stand longer than eight to ten hours, whereas if necessary the finished blue, for filtering, will keep in the unpressed state for twelve to fourteen hours (but not longer) without change.

The pressed colour in the drying-stove does not turn if the temperature there is not higher than 35° C., though at a higher temperature it blackens very easily. When, however, the product has been about half dried at 35° C., the drying process can then be accelerated, without any disadvantage to the beauty of the product, by increasing the temperature to 55° C.

Direct Method

Since, with the present high prices of raw materials, the manufacture of Bremen blue is only profitable when very great quantities are made, correspondingly large vessels are necessary for quick and easy working. This applies chiefly to the tank used for washing the finished blue. In view of the damage caused to the shade of the pigment by delay in washing, this tank must be as large as possible in order to accelerate the operation by using large quantities of water.

Of no less importance is the suitable size of the vessels used for preparing and storing the alkali solutions. The most suitable for this purpose are two large enamelled cast-iron pans of different sizes, placed close to the working tanks, so that there is always a supply of ready made solution available. The larger pan is reserved for dissolving caustic soda exclusively, whilst the smaller pan serves for diluting the solution with water to the prescribed degree of concentration. To allow the solutions an opportunity of cooling during the night, the caustic soda is preferably dissolved in the evening. Concentrated solutions (40° to 45° B.) are desirable, both because concentrated solutions, being less voluminous, will cool much quicker, and, on the other hand, in the solution from 40° to 10° B. a very large quantity of cold water is required, so that the reduction of the soda lye to the prescribed temperature is more certainly secured even when, from any cause, it has been impossible to cool the strong lye beforehand. On the other hand, much larger quantities of the more or less dilute liquors can naturally be obtained from highly concentrated caustic solutions than from weaker solutions; and it is important in the manufacture of Bremen blue to have a certain stock of soda lye, to save time in case of a sudden emergency.

Moreover, a second tank is needed for precipitating the copper salt with the soda lye.

Apart from metallic copper, the only raw material now used in the manufacture of all copper colours is copper sulphate, $CuSO_4 + 5H_2O$. When a solution of copper sulphate is treated with soda lye, until the precipitate ceases to increase, basic copper sulphate of varying composition is obtained in the form of a voluminous bluish-green precipitate, which shrinks considerably in drying and forms a fairly dense apple-green powder. On treating the wet basic copper sulphate, after removing the colourless liquid, with the same solution of caustic soda, the basic compound is deprived of the last trace of sulphuric acid, sodium sulphate being formed, and copper hydroxide, $Cu(OH)_2$, of a magnificent blue shade is obtained.

This reaction forms the basis of the manufacture of Bremen blue, which is therefore divided into two stages, viz.:

1. The formation of basic copper sulphate by precipitating a cold solution of copper sulphate with a cold solution of caustic soda, density 10°.
2. Toning the pale green basic copper sulphate blue with caustic soda lye, density 28° to 32°.

First Stage.—The work begins in the morning with dissolving the calculated quantity of perfectly iron-free Swedish copper sulphate in a minimum of hot water in the smaller tank, and adding cold water until the temperature has fallen to 15° to 20° C. Into this solution is run, with constant stirring, a thin stream of the cold 10° caustic soda lye until a precipitate ceases to form and the blue liquid is completely decolorised. For practical reasons an excess of caustic soda must be avoided, and the same applies, on economic grounds, to the copper sulphate, so that the quantities must be determined exactly. This can be done approximately by calculation and determined with absolute accuracy as follows: When the reaction is almost completed small samples of the mixture are dropped on white filter paper. The wet zones formed around the spots are touched with a glass rod which has just previously been dipped in a dilute solution of potassium ferrocyanide. The formation of a brownish-red stain of copper cyanide at the point of contact shows that the copper sulphate has not yet been completely precipitated by the caustic soda. By repeating the test the brown-red coloration grows less and less distinct in proportion as the amount of copper left in the solution of copper sulphate decreases, so that with a little practice the end point of the precipitating process can be ascertained with perfect accuracy. This being done, the addition of caustic soda must be stopped, though stirring must be continued at least a quarter of an hour longer. The apple-green precipitate is next allowed to settle down, which will take one and a half to two hours, whereupon the mother liquor is drawn off.

Second Stage.—The precipitate of basic copper sulphate thus obtained must now be converted into pure copper hydroxide, the Bremen blue of commerce. This is effected with the cold solution of (28° to 32°) caustic soda, the apple-green colour of the precipitate turning to a bright sky blue. For this purpose the aforesaid caustic soda lye is added, a pailful at a time, with continual stirring, and as quickly as possible, samples being drawn at frequent intervals to see if the blue toning is progressing. For this purpose some of the blue colour is dropped on to white filter paper, waiting a few seconds until the latter has absorbed the colour evenly. A glass rod is then dipped in the solution of caustic soda (28° strength), and applied to the colour on the filter paper. If the blue colour is deepened, more caustic soda must be added; if not, the operation is terminated and the finished product is put into the washing tank, which is filled two-thirds full with pure cold water. A quick, but careful, washing is given three times at least. Since everything depends on the caustic soda being added very quickly, and on the colour being left for only a minimum period in contact with the alkali, the best way to obtain products of uniform shade is to note how much alkali was used on the first occasion a really handsome shade was obtained, so as to have in this way an approximate guide for subsequent batches. Of course, it is assumed in this case that the same vessels and the same strength of alkali are used on both occasions.

The washed blue is filtered, pressed, cut into oblong cakes, and dried at a moderate temperature (about 35° C.) in heated drying-rooms. In this state the best made Bremen blue is of remarkable low density, the latter varying inversely with the brightness of the colour. For this reason all consumers lay great stress on low specific gravity when buying this article.

In spite of the use of a proper temperature in drying, the Bremen blue may turn black, or at least dark-coloured, in which event it has not been washed with sufficient care, the changes in question being caused by the action of residual caustic soda in abstracting water and transforming the copper hydroxide into black copper oxide. When this occurs the product can be worked up again into copper sulphate by dissolving it in a suitable quantity of sulphuric acid. Forty parts of Bremen blue will be obtained from 100 parts of crystallised copper sulphate and 53 parts of commercial (solid) caustic soda.

Indirect Method

In this method the basic compound is prepared from metallic copper in the form of scrap sheet copper of any kind, as well as copper sulphate. The raw material for producing the copper hydroxide is not basic copper sulphate, but basic copperoxide-copperchloride, is most cheaply obtained in the following manner:

Of finely ground copper sulphate 222 parts are thoroughly mixed with 225 parts of dry common salt, preferably in a large ball mill, the mixture being moistened to form a very stiff paste, which is put through a roller mill to obtain uniform consistency. The two salts undergo double displacement, copper chloride and Glauber salt (sodium sulphate) being formed.

$$\underbrace{CuSO_4}_{\text{Copper sulphate}} + \underbrace{2NaCl}_{\text{Common salt}} = \underbrace{CuCl_2}_{\text{Copper chloride}} + \underbrace{Na_2SO_4}_{\text{Glauber salt.}}$$

This mixture is incorporated with the finely cut and cleansed sheet copper. The scrap sheet copper, after being cut into equal pieces, is cleaned in tightly closed barrels by treating it with dilute caustic soda and rolling the barrels for some hours. The barrels are then opened, the caustic soda solution is drawn off into a vessel underneath, for use over again with a fresh batch of scraps. The cleansed scraps are next thoroughly washed with warm water, and treated with dilute sulphuric or hydrochloric acid, the barrels being rolled continually for another ten to twelve hours at least. The constant movement scours the small scraps and makes them perfectly bright. The acid being drawn off, the material is washed and drained, whereupon the scrap metal is ready for use. The above quantity of common salt and copper vitriol must be mixed with 225 parts of washed scrap copper—*i.e.*, exactly the same weight as that of the common salt.

To form basic copper oxychloride the cupric chloride obtained by the above process must be left to react on the metallic copper for some considerable time in the presence of air. In this reaction the cupric chloride first takes up copper, and is changed into cuprous chloride, which latter is converted into the insoluble green basic compound by taking up oxygen (from the air) and water (from the moisture present). This process may tak weeks, or even months, to complete. The mixture must be spread out to depth of about one inch, in shallow oaken oxidation boxes, entirely fre from iron fittings. The layers must be turned over thoroughly every tw to three days, by means of copper or wooden shovels, to accelerate th reaction by admitting sufficient oxygen. The main point for ensurin favourable results is to make sure that the basic compound does not contai the slightest trace of cuprous chloride. In the subsequent treatment wit caustic alkali this would form yellow or red cuprous oxide, which would spoil the purity of the resulting shade of Bremen blue. Hence special care must be taken to turn the masses in the oxidation boxes thoroughly and at regular intervals all through this stage of the process. The oxidation boxes are placed in a room where a moderate but invariable temperature is maintained—*e.g.*, in a cellar—and the mass turned over as prescribed; the oxidation will generally be finished in three months, and the formation of the basic copper oxychloride will be complete. This can best be ascertained by rubbing a small quantity of the product in a mortar with a large quantity of water, and dropping some of this mixture upon filter paper. The potassium ferrocyanide test should give the same results as mentioned in the direct process—*i.e.*, no red copper cyanide will be formed when the operation is complete. When all the cuprous chloride has passed into the basic compound the next step is to separate the unoxidised particles of copper from the light green mass, preferably by levigation. For this purpose the mixture is placed in a cleaning tank and thoroughly stirred up with pure water, the green liquid, containing suspended basic copper oxychloride, being drawn off from the metallic copper, which has settled down to the bottom. The liquid is passed through a fine silk sieve so as to also retain the smallest copper particles, which settle down more slowly. After washing the apple-green sediment several times it is filtered and allowed to drain completely.

The sediment may still contain very minute particles of metal, that will traverse even the finest sieve, and these may prove very troublesome afterwards in the dried blue. To remove these as well a certain quantity of hydrochloric acid is added to the precipitate, whereby the copper is converted into the basic compound in three to four days. For 30 parts of moderately stiff paste about ½ to 1 part of hydrochloric acid (21° B.) will be required. At the expiration of this period the mass is washed again, once or twice, and finally filtered. To make sure of getting a compound free from cuprous salts, the precipitate must remain in the wet state on the filter for one or two weeks longer, during which time any residual cuprous oxide will be certainly converted into cupric oxide, and the subsequent toning process will be sure to result favourably.

This somewhat protracted method is, however, not absolutely essential, since the blueing of the precipitate, acidified with hydrochloric acid, can be effected after the precipitate has stood for the prescribed time—even without washing and filtering—in the manner already explained in the direct process. But in this case the absence of cuprous oxide must be determined by exact analysis. When the precipitate has been exposed to a second oxidation process it must be stirred up again with water before blueing, in order to prevent unequal colouring through the formation of lumps.

The blueing can be performed in two ways, according as stronger or weaker caustic soda lye is used. In the first case the procedure is exactly as described in the direct process; but in the other case the operation is just reversed. The precipitate, finely distributed in water, is measured off in pails, each 5 parts by volume being treated with 11 parts of caustic soda (20° B.). This lye is poured into the toning vat, and the described proportion of basic copper oxychloride is added at once. After stirring for two hours the whole is left to stand twenty-four to thirty-six hours, and is then washed, filtered, pressed, and dried at 35° C.

Both methods give the same result, but the former is decidedly preferable on account of its simplicity.

For adding gypsum, ground pumice-stone, diatomaceous earth, &c., to the Bremen blue to produce cheaper brands, these adjuncts are incorporated in the usual manner before filtering the toned and washed colour. Pure Bremen blue is readily soluble in acid.

2. Lime Blue, Mountain Blue, Neuwied Blue

Although these colours are now very rarely met with in commerce, and therefore manufactured only in very small quantities, they are sufficiently interesting to justify a brief description.

Lime Blue, which is now replaced by the far more powerful and equally permanent lakes from coal-tar colours, was formerly prepared by different methods, of which the following was the most popular and reliable. In this method iron-free copper sulphate also serves as the raw material, and the difference between this process and that used for Bremen blue consists in carrying out the precipitation with caustic lime of the purest—*i.e.*, whitest—grade, instead of caustic soda. 125 parts of copper sulphate are dissolved in hot water, and the solution diluted with cold water until the density sinks to 5° B. Hereupon 30 parts of purely fresh, burned lime are made into a moderately thick paste, which is left for a few days and frequently turned, so that all the particles of lime are thoroughly slaked. More water is then added, and the resulting milk of lime is forced through a fine brass sieve, to remove any coarse impurities, sand, gravel, &c. The sifted milk of lime is reground in a wet mill or an ordinary funnel mill, to make it perfectly homogeneous. Meanwhile 13 parts of ammonium chloride are dissolved in hot water, and this solution is added to the copper sulphate solution and stirred up together. The reason for adding ammonium chloride will be explained later on. All is now ready for precipitating the lime blue. This is effected by thoroughly stirring the still further diluted milk of lime into the solution of copper sulphate as quickly as possible whereupon the blue colour will form at once. After the precipitate has settled down the solution exhibits a deep blue shade and a distinct smell of ammonia, both, however, disappearing after the mass has stood two to three days. The supernatant liquid will then be as limpid as water, a sign that the reaction is finished and the colour ready. It is washed in the same vat three or four times with pure cold water, filtered, pressed, and dried at 35° C.

The part played by the sal ammoniac in this process consists in the reaction with lime to form calcium chloride and free ammonia. The latter dissolves the slightest traces of copper salts, and thus gives a characteristic beautiful blue shade (ammoniacal copper oxide) which constitutes an indication of the presence of copper salts. Now it has been thought that a brighter coloured product could be obtained by producing ammonia during the formation of the blue copper colours. This is, however, not the case, for the aforesaid blue colour of the ammoniacal solution of copper salt exists only so long as ammonia is present. The increased brightness of the blue copper colours, obtained by the aid of ammonia, will disappear on drying, owing to the volatilisation of the causative agent, ammonia. The bright blue supernatant liquid loses its colour after a few days. The reaction in this process will be easily understood from what has been already stated. The copper hydroxide kept in solution by the presence of ammonia is precipitated from the solution in proportion as the ammonia evaporates (on leaving the vessel uncovered), whereupon the loss of colour naturally ensues. The addition of sal ammoniac seems, therefore, to be quite superfluous. In fact, the process will succeed just as well without any sal ammoniac, the resulting shade being quite as bright.

When lime blue, usually sold in the form of powder, is made up into oblong rectangular lumps it is known as *Neuwied blue*, no doubt with the idea of making consumers believe that it is a different article. Lime blue, which, as its name indicates, was formerly used as a lime colour exclusively, has very little colouring power, and is of no value at all as an oil colour.

Mountain Blue.—The endeavour to imitate by artificial means the native basic copper carbonate (mountain blue), which has a magnificent bright blue shade, but is very dear, owing to its rarity, has resulted in a number of processes. These have all proved failures, for, as a fact, no copper colour has yet been put on the market with the composition or even the brilliant appearance of natural mountain blue. Of all these many processes we will only mention one, which, though it does not furnish basic copper carbonate, nevertheless gives a specially brilliant colour, and therefore, in spite of its clumsiness, merits some consideration. As raw material for this process use is made of cupric chloride, prepared by treating copper sulphate with calcium chloride. 125 parts of copper sulphate are dissolved in 150 parts of hot water, the solution having a density of 35° B. 160 parts of solid calcium chloride are dissolved in 40 parts of hot water, giving a 40° B. solution, which is used to precipitate the solution of copper sulphate, the mixture being kept well stirred. The chemical reaction between the two salts will form cupric chloride, and calcium sulphate (gypsum) settle down to the bottom quickly as a solid body when stirring is discontinued. The solution of cupric chloride is separated from the gypsum by filtering, and the latter then washed once, the washings being united with the main solution. This is next divided equally among four tanks, each holding about 100 gallons, for further treatment, to produce basic copper oxychloride. For this purpose 100 parts of quicklime are slaked with thrice that quantity of water, and the resulting lime paste is worked in exactly the same manner as already described for lime blue. When a very finely distributed state has been attained it will be ready for use. Four portions, each of 20 parts, are weighed out and added to four portions of the cupric chloride solution, the whole being well mixed. A sample of the precipitate is drawn from the solution and tested for the presence of copper (with potassium ferrocyanide). If copper is found by this test more lime must be added and the test repeated until all the cupric chloride has been converted into basic copper oxychloride. Calcium chloride is formed in solution at the same time, and must be separated from the green precipitate by decantation and filtration. After being concentrated to a density of 40° B., the calcium chloride liquor can be used again for precipitating a fresh batch of copper sulphate. It is not quite clear why Payen, to whom this method is due, divides the resulting cupric chloride into four parts for precipitation with calcium hydroxide, as this arrangement causes troublesome delay in working, whereas the precipitation can be carried on just as well at once and in much less time without affecting the result.

The basic copper oxychloride having been obtained in this manner, must now be converted into the blue compound, which can only be done by stages. For this purpose it is first of all necessary to know the percentage of water in the green pasty sediment. A small quantity, about 100 grm., is weighed out and dried; the difference between the first and final weights gives the percentage of water in the paste. Next a sufficient quantity of the precipitate must be weighed to furnish 22 lbs. of dry matter, which is spread out in a tub and treated with 2¾ lbs. of the above milk of lime, well stirred in, followed at once by 1¾ pints of a 15° B. solution of potash, also kept well stirred. Finally the blue mass is ground in a funnel mill to obtain a uniform shade. In the meanwhile 1¼ lbs. of copper sulphate are dissolved, and half that quantity of sal ammoniac, each separately in seven pints of water. These two solutions are added to the colour after the latter has left the mill. Each portion is filled into a large bottle, and kept three to four days hermetically closed. The rest of the stock of green paste is treated in the same manner.

Four days later all the bottles must be opened, their contents poured into a vat, and the whole mass washed three or four times with cold water, filtered, pressed, and dried.

On considering this process more closely, the blueing with potash and lime seems to rest, at least to some extent, upon the action of the liberated caustic potash. The subsequent addition of copper sulphate seems merely for the purpose of compensating the excess of caustic potash, which is liable to be formed under the somewhat haphazard system necessarily adopted in view of the always unknown quantity of active potash present. Therefore the blueing of the green precipitate can also be directly performed with a strong solution of caustic soda, as mentioned in the case of Bremen blue. In fact, the same product will be obtained both in appearance and composition; for neither the addition of potash nor the useless action of the sal ammoniac justifies the supposition that Payen's method will furnish basic copper carbonate—*i.e.*, a product equivalent to natural mountain blue. Nevertheless it gives a very good shade of colour, and the cheap method of preparing basic copper oxychloride (owing to the recovery of part of the calcium chloride) is worthy of note.

Mention may be made briefly of the so-called *Oil blue*, copper monosulphide, CuS, of a very pretty bright blue shade. It is, however, very sensitive, and can be worked only with linseed varnish, which forms a protective envelope for the colour. It is obtained by putting fine copper filings or wire scrap, free from oxide, into boiling sulphur until very little excess of sulphur remains. This operation is performed in glass retorts, which must be smashed when the process is finished. The cake of colour obtained in this manner must be boiled with caustic soda to remove the final traces of sulphur. If the operation has been properly carried out the mass shows a pure blue shade throughout. Black patches appear in the mass when too much copper has been used.

Copper hydroxide obtained by simply precipitating copper sulphate with caustic soda in cold solution is used by decorators as a water-colour.

Generally speaking, however, the blue copper colours are of no practical importance to-day.

b. BLUE FERROCYANIDE COLOURS

Prussian Blues (*Berlin and Paris Blue*)

The manufacture of this extremely important group of colours is becoming more and more restricted to special blue works, or the very largest general colour manufactories, on account of the very extensive plant required and the fact that the process is only profitable when carried out on a large scale. The extremely fine state of division necessary for the different precipitates in order to obtain products capable of holding their own on the market requires very large tanks, whilst for the same reason the finished colours settle down very slowly indeed in the washing process, which for these colours has to be repeated more frequently than with any others, this stage often taking weeks to complete. On the other hand, the filtering and even the pressing of the washed colours are rendered very troublesome and protracted operations.

Owing to the difficulties of the manufacturing process, it is necessary in order to be able to turn out a certain quantity of colour at regular intervals to have a very extensive plant, so that several operations can be performed simultaneously. This applies particularly to the washing of the colours, for which purpose the number of washing tanks must be increased in order to maintain continuity of production. This naturally implies a considerable increase in working space; and if in addition the high price of the most important raw materials be borne in mind, it is evident that large capital is needed for carrying on such a business profitably—a circumstance sufficiently explaining the existence of special factories for making these colours.

The raw material used in the manufacture of Prussian blue is the yellow prussiate of potash (potassium ferrocyanide), K_4FeCy_6. The colour is formed direct by precipitation with a ferric compound. The ferric salts most largely used for this purpose are ferric sulphate, $Fe_2(SO_4)_3$, and ferric chloride, Fe_2Cl_6, both readily soluble salts. The chemical reaction occurring in the precipitation is explained by the following equations:

$$1.\quad \underbrace{3K_4FeCy_6}_{\text{Potassium ferrocyanide}} + \underbrace{2Fe_2(SO_4)_3}_{\text{Ferric sulphate}} = \underbrace{Fe_7Cy_{18}}_{\text{Prussian blue}} + \underbrace{6K_2SO_4}_{\text{Potassium sulphate}};$$

Or

$$2.\quad \underbrace{3K_4FeCy_6}_{\text{Potassium ferrocyanide}} + \underbrace{2Fe_2Cl_6}_{\text{Ferric chloride}} = \underbrace{Fe_7Cy_{18}}_{\text{Prussian blue}} + \underbrace{12KCl}_{\text{Potassium chloride}}.$$

The Prussian blue (potassium ferri-ferrocyanide, $3FeCy_2 + 4FeCy_3 = Fe_7Cy_{18}$) obtained by this method is also known as neutral Prussian blue.

The same product is obtained indirectly by precipitating ferrous salts with potassium ferrocyanide and oxidising the resulting white precipitate of ferrous ferrocyanide with any suitable oxidising agent. Whether, however, the precipitate known as "white paste" is really ferrous ferrocyanide is not at all certain. Ferrous sulphate $FeSO_4.7H_2O$ is almost the only soluble ferrous salt used for this method, ferrous chloride $FeCl_2$ being also, though rarely, employed. The formation of the ferrous ferrocyanide is explained (if it really occurs at all) by the following equations:

$$1.\quad \underbrace{K_4FeCy_6}_{\text{Potassium ferrocyanide}} + \underbrace{2FeSO_4}_{\text{Ferrous sulphate}} = \underbrace{Fe_2FeCy_6}_{\substack{\text{Ferrous ferro-}\\ \text{cyanide}}} + \underbrace{2K_2SO_4}_{\text{Potassium sulphate};}$$

Or

$$2.\quad \underbrace{K_4FeCy_6}_{\text{Potassium ferrocyanide}} + \underbrace{2FeCl_2}_{\text{Ferrous chloride}} = \underbrace{Fe_2FeCy_6}_{\substack{\text{Ferrous ferro-}\\ \text{cyanide}}} + \underbrace{4KCl}_{\text{Potassium chloride.}}$$

A number of oxidising agents can be used for oxidising the white precipitate of ferrous ferrocyanide, $3(FeCy_2) = Fe_2FeCy_6$, but in practice these are restricted to such as are cheap and at the same time give the brightest shades. The following are mostly used:

1. Sulphuric and nitric acids.
2. Ferric sulphate.
3. Ferric chloride.
4. Chlorine (bleaching-powder and hydrochloric acid), nitro-hydrochloric acid (aqua regia).
5. Potassium bichromate and sulphuric acid.
6. Potassium chlorate and hydrochloric acid.

It may also be remarked that persulphuric acid produced by the electro-chemical process might be a useful oxidising agent, as also the perchlorates. It is, perhaps, not impossible to use the electrical current directly for the same purpose. In all cases the chemical reaction is based on the oxidising agent taking away two atoms of iron from three molecules of Fe_2FeCy_6, and forming the corresponding ferrous salt, together with the deep indigo-blue ferric ferrocyanide (Prussian blue). The following equations represent the reactions occurring with the aforesaid oxidising agents:

1. With sulphuric and nitric acids—

$$\underbrace{3Fe_2FeCy_6}_{\text{White precipitate}} + \underbrace{2H_2SO_4}_{\text{Sulphuric acid}} + \underbrace{4HNO_3}_{\text{Nitric acid}}$$

$$= \underbrace{Fe_7Cy_{18}}_{\text{Prussian blue}} + \underbrace{2FeSO_4}_{\text{Ferrous sulphate}} + \underbrace{4H_2O}_{\text{Water}} + \underbrace{4NO_2}_{\text{Nitrous acid.}}$$

2. With ferric sulphate—

$$3Fe_2FeCy_6 + \underbrace{2Fe_2(SO_4)_3}_{\text{Ferric sulphate}} = \underbrace{Fe_7Cy_{18}}_{\text{Prussian blue}} + \underbrace{6FeSO_4}_{\text{Ferrous sulphate.}}$$

3. With ferric chloride—

$$3Fe_2FeCy_6 + \underbrace{2Fe_2Cl_6}_{\text{Ferric chloride}} = \underbrace{Fe_7Cy_{18}}_{\text{Prussian blue}} + \underbrace{6FeCl_2}_{\text{Ferrous chloride.}}$$

4. With chlorine—

$$3Fe_2FeCy_6 + \underbrace{4Cl}_{\text{Chlorine}} = \underbrace{Fe_7Cy_{18}}_{\text{Prussian blue}} + \underbrace{2FeCl_2}_{\text{Ferrous chloride.}}$$

5. With potassium bichromate and sulphuric acid—

$$3Fe_2FeCy_6 + K_2Cr_2O_7 + 7H_2SO_4 = \underbrace{Fe_7Cy_{18}}_{\text{Prussian blue}}$$

$$+ \underbrace{2FeSO_4}_{\text{Ferrous sulphate}} + \underbrace{2KHSO_4}_{\text{Potassium bi-sulphate}} + \underbrace{Cr_2(SO_4)_3}_{\text{Chromic sulphate}} + 7H_2O.$$

6. With potassium chlorate and hydrochloric acid—

$$3Fe_2FeCy_6 + \underbrace{KClO_3}_{\text{Potassium chlorate}} + \underbrace{6HCl}_{\text{Hydrochloric acid}} = \underbrace{Fe_7Cy_{18}}_{\text{Prussian blue}}$$

$$+ \underbrace{2FeCl_2}_{\text{Ferrous chloride}} + \underbrace{Cl_2}_{\text{Chlorine}} + \underbrace{KCl}_{\text{Potassium chloride}} + 3H_2O.$$

The resulting ferrous chloride is probably converted at the moment of formation directly into ferric chloride by an excess of chlorine. Prussian blue manufactured according to one of the foregoing methods is termed basic Prussian blue by some manufacturers (in contrast to the neutral blue mentioned above), but how far this is correct we need not inquire.

Although direct precipitation of soluble ferric salts seems to be the easiest and most convenient way of making the different brands of Prussian blue, the other is preferred in practice. In this, the indirect process, ferrous salts are used as the raw materials, since the resulting products, even though of the same chemical composition as those from the other process, are not only of a purer blue shade, but also exhibit a far more metallic lustre, on account of their much finer structure. This lustre is regarded by consumers as the prime and most distinctive characteristic of pure Prussian blue, and is always demanded in the case of the best grades.

Indirect Methods of making Prussian Blue.

The first operation to be performed in this process is the formation of the white precipitate of ferrous ferrocyanide, Fe_2FeCy_6, in a perfectly pure state, *i.e.*, in an unoxidised condition, since otherwise, as experience has shown, it is impossible to obtain a perfect product. Now, as ferrous ferrocyanide is oxidised on exposure to atmospheric oxygen, the foregoing condition is difficult of fulfilment, and it is naturally quite impossible to protect the white precipitate completely against the influence of the air during the prolonged treatment it has to undergo. Ferrous ferrocyanide acquires a bluish-green shade on the slightest oxidation, and therefore its freedom from oxidation can be reliably assumed when it remains pure white—a condition which it is the aim of the manufacturer to maintain as far as possible. For this purpose the ferrous salts used must be perfectly free from ferric compounds. On the other hand, however, a considerable part is played by the water used. Thus it is known that ordinary river or well water contains in solution a certain quantity of air, which is expelled by continued boiling. We have thus two very important factors in the production of ferrous ferrocyanide, viz., pure ferrous salts and boiling water entirely deprived of air.

As already mentioned, commercial ferrous sulphate only is used for manufacturing Prussian blue by the indirect process. This material can be bought at such a low price that there is no advantage in making it oneself. In the pure state this salt forms bluish-green crystals of different sizes, but the commercial article is usually in the form of yellowish-green fragments or lumps. This striking deviation from the normal shade is due to free ferric oxide, with which the commercial salt is always contaminated. On dissolving the salt in hot water this ferric oxide is precipitated, after longer standing, in the form of a yellowish sediment, which can, however, be reconverted into green ferrous sulphate by adding a corresponding quantity of sulphuric acid to the solution. This circumstance enables a solution of ferrous sulphate to be obtained perfectly free from ferric compounds.

The precipitation of the ferrous sulphate solution is effected by means of the following plant: First of all, two tanks of equal size, measuring at least 4 ft. in diameter and 4½ to 5 ft. in height, and made of 2- to 3-inch pine, are required for making the solutions of ferrous sulphate and potassium ferrocyanide. These two tanks must be placed close together above the precipitation tank in such a way that their contents can be transferred into the latter easily and without loss. The precipitation tank must therefore be as large as the two dissolving tanks, and is preferably of still larger size, in order to maintain the white precipitate in a very finely divided state. It is advisable to provide the precipitation tank with a mechanical stirring appliance. The two smaller high-level tanks are filled about three-fourths full with pure water, and this is heated to boiling by admitting direct steam for fifteen to twenty minutes. Then 180 lbs. of ferrous sulphate are dissolved in one, and 200 lbs. of potassium ferrocyanide in the other, by continued stirring, and without shutting off the steam. For reasons already given, 1 to 1½ lbs. of sulphuric acid must be added to the ferrous sulphate solution, both liquids being then allowed to stand for some time, to enable the ever-present mechanical impurities, such as sand, carbon, wood particles, &c., to settle down. The precipitation tank (if its dimensions will allow) must be filled about a quarter full with pure water, that is also kept boiling for a long time.

As soon as the solutions of ferrous sulphate and potassium ferrocyanide have clarified sufficiently the former is run into the precipitating tank, but without carrying with it any of the sediment, and the ferrocyanide solution is added as a very thin stream, the stirrers being set going at the same time. After stirring for about a quarter of an hour the formation of ferrous ferrocyanide may be considered as complete. The final temperature of the liquid in the precipitation tank should not be less than 80° C., preferably higher. The resulting precipitate, which, if everything has been done properly, will be perfectly white, must then be washed out at least twice with hot water before being oxidised. It is left at rest for thirty-six to forty-eight hours to settle down. The washing is performed in the usual manner, care being taken that the temperature of the water is from 60° to 70° C.

For the oxidation process the white precipitate must be formed into a very stiff paste, with which object the ferrous ferrocyanide is filtered in baskets, or the superfluous water is expelled by evaporation. The latter method, though more expensive, is preferable, since it lessens the risk of premature oxidation by the air. A still better plan, however, is to fill the thin, pasty precipitate by portions into the box of a large wooden press, lined with a press cloth (Fig. 15), the superfluous water being expelled under pressure by gradually tightening the pressure of the screw. This operation takes some time, but is much quicker than filtering, cheaper than the evaporating process, and excludes air almost entirely. The pressed paste must be thick enough to bear lifting with a flat steel shovel without slipping off from the latter. If too strongly pressed the paste becomes sticky, which should be avoided, as it makes stirring difficult during oxidation, and thus delays the process.

The *modus operandi* of oxidation differs considerably according to the peculiarities of the oxidising agents used. The oldest and most imperfect method of oxidation, by treating the ferrous ferrocyanide paste with atmospheric oxygen, is no longer practised, and need not be described. Though the sulphuric and nitric acid method seems also to have gone out of use, or is very seldom employed in large works, it may be discussed briefly.

1. *Oxidation with Sulphuric and Nitric Acids.*

For every 100 parts of yellow prussiate, 90 of ferrous sulphate (copperas), 40 of sulphuric acid (66° B.), and 75 of nitric acid (40° B.) are employed.

The ferrous ferrocyanide paste, treated as described, is placed in a tank of medium size and stirred as thoroughly as possible. The tank must be placed out of doors, or at least in a very airy room, and fitted with a steam pipe for heating the contents. When the paste has acquired uniform consistence, under prolonged stirring, the weighed sulphuric acid is added, and a perfect mixture obtained by stirring afresh. This work is somewhat difficult, but must be performed thoroughly. This done, steam is admitted without stopping the stirrers, gradually at first, but increasing progressively, until the mass in the tank has been raised to about 80° to 90° C. This is the suitable moment for adding the nitric acid as quickly as possible. The cold nitric acid causes the mass to cool, and steam must therefore be admitted afresh, with constant stirring, until the mixture has regained its former temperature. The beginning of the reaction is indicated by the appearance of an indigo shade, the mass then frothing up and liberating yellowish fumes of nitrous acid. As soon as these appear the stirring is interrupted, but the steam is turned on again. The evolution of nitrous acid, escaping in brownish-red vapours, increases in violence as the reaction progresses. The fumes of this acid being very poisonous, care must be taken that they are not inhaled, this being specially dangerous when the work is carried on in insufficiently ventilated rooms. Generally the most convenient plan is to provide the oxidation tank with a tight-fitting hood, through which the nitrous fumes are conducted into the open air by means of a wide pipe projecting some distance above the roof of the workroom. Glass peepholes, suitably placed with regard to the light, allow the progress of affairs inside the tank to be observed. By this means the whole process can be kept under proper control without any danger to the workmen. When the fumes diminish the steam valve is closed, but the contents of the tank are kept carefully stirred until the fumes cease to escape, whereupon the reaction is terminated, the contents of the tank being afterwards heated to boiling-point.

The colour after standing twenty-four hours in the covered tank is ready for washing. This is the most troublesome operation of all, and should be performed in large tanks to accelerate matters. Hot water must be used throughout. The washing tank is filled with hot water so as to leave plenty of room for the Prussian blue paste, the whole being stirred for about fifteen to twenty minutes and left to settle down. The washing must be repeated until barium chloride no longer reveals the presence of sulphuric acid in the washings, or produces merely a faint turbidity. It is necessary to renew the washing water ten to twelve times, according to the dimensions of the washing tank. The blue is then filtered and pressed in the ordinary manner, cut into small pieces 2 ins. long and ¾–1 in. thick, and dried first at a low heat and afterwards at a higher temperature (60° to 70° C.). The drying-stoves used for this purpose must be perfectly free from dust. As a rule, Prussian blue will have a greater lustre the higher the temperature maintained in drying, though this does not apply to all brands. The Prussian blue obtained by this method has a tone similar to indigo.

2. *Oxidation with Ferric Sulphate*

Ferric sulphate, not being a commercial article, must be produced in the works. There are different methods of producing it, but only two will be considered here as being the most suitable for the process in view. The first method, depending upon the oxidation of ferrous sulphate to ferric sulphate by sulphuric and nitric acid, is the more simple and more convenient; whilst the second, which consists in dissolving ferric oxide, Fe_2O_3 (colcothar, caput mortuum) in sulphuric acid, is the cheaper.

First Method.—In a tank of moderately large size 276 parts of commercial ferrous sulphate are dissolved in 500 to 600 parts of boiling water. 50 parts of sulphuric acid (66° B.) are added in a very thin stream, with constant stirring, and very carefully, to prevent injury from the spurting of the hot liquid. Nitric acid (40° B.) is next run in, with continued stirring, as long as the liquid continues to froth up and disengage the brownish-red fumes of nitrous acid. The latter must be led away in the manner already described. Stirring is continued for a short time after the disappearance of the nitrous fumes indicates that the reaction is ended. The ferric sulphate is then ready for use. An excess of one or other of the acids is immaterial. The formation of ferric sulphate takes place according to the following equation:

$$\underbrace{2\mathrm{FeSO_4}}_{\text{Ferrous sulphate}} + \underbrace{\mathrm{H_2SO_4}}_{\text{Sulphuric acid}} + \underbrace{2\mathrm{HNO_3}}_{\text{Nitric acid}}$$

$$= \underbrace{\mathrm{Fe_2(SO_4)_3}}_{\text{Ferric sulphate}} + \underbrace{2\mathrm{NO_2}}_{\text{Nitrous acid}} + \underbrace{2\mathrm{H_2O}}_{\text{Water.}}$$

Second Method.—140 parts of red ferric oxide (pure colcothar, caput mortuum, &c.) is made into a paste with water, preferably in a cast-iron pan, and 240 parts of sulphuric acid are then added, the whole being well stirred with an iron shovel. After a short time the mixture becomes hot, white, and finally sets to a solid mass, which after twenty-four to thirty-six hours is crushed and dissolved in 600 to 800 parts of water in another cast-iron pan over a fire. Only a small quantity of ferric oxide remains undissolved as a rule. The insoluble ingredients are allowed to settle down, and the clear liquid is used. The chemical reaction in this method is explained by the following equation:

$$\underbrace{Fe_2O_3}_{\text{Ferric oxide}} + \underbrace{3H_2SO_4}_{\text{Sulphuric acid}} = \underbrace{Fe(SO_4)_3}_{\text{Ferric sulphate}} + \underbrace{3H_2O}_{\text{Water.}}$$

Solutions of ferric sulphate must be used in a concentrated state only, since they decompose when diluted too far with water, especially at higher temperatures, forming a basic light yellow salt of iron (insoluble in water) and free sulphuric acid.

The oxidation of ferrous ferrocyanide with soluble ferric salts has the advantage that the white precipitate need not be in the form of a paste—*i.e.*, has not to be filtered or pressed—but can be used in the state in which it is obtained from the washing process, after thoroughly removing the washing water. All that need be done, therefore, is to heat the precipitate in the tank by direct steam, and continue to add the concentrated ferric sulphate solution so long as the Prussian blue precipitate increases in brightness, samples being taken at intervals for comparison. The reaction is considered as finished when the presence of an excess of ferric sulphate can be detected in addition to ferrous sulphate in the filtrate. The latter should give a dark blue precipitate with a solution of potassium ferrocyanide. The test can be applied in a still simpler way by dropping a small quantity of the Prussian blue from a glass rod on to white filter paper. The gradual appearance of a yellowish edge around the stain indicates an excess of ferric sulphate. There is no advantage in having any great excess, and, indeed, this should be avoided for economic reasons. After thirty minutes' stirring the mixture is allowed to stand twenty-four hours, afterwards washed out, pressed, and dried in the manner already described.

3. *Oxidation with Ferric Chloride*

The process of colouring ferrous ferrocyanide with ferric chloride is very similar, the latter being made (if not purchasable) by dissolving ferric oxide with commercial nitric acid (21° B.).

4. *Oxidation with Chlorine*

The brightest Prussian blues are undoubtedly obtained by the oxidation of ferrous ferrocyanide with chlorine. These are not only of bright indigo shade with a slight reddish tint, but they also exhibit the highest metallic coppery lustre of any. Since the direct preparation of chlorine and its subsequent introduction into the liquid containing the precipitate is too expensive on account of the apparatus required, this method is only seldom practised. Generally such materials are used as are capable of liberating free chlorine, which in the nascent state exerts an oxidising effect on the ferrous ferrocyanide. To these bodies belong bleaching-powder and commercial hydrochloric acid, nitrohydrochloric acid (aqua regia), potassium chlorate, and hydrochloric acid. The best method of applying these agents will now be described.

Owing to the powerful action of chlorine it is unnecessary to filter or press the white paste, this being merely left to settle down as compactly as possible and the washing water drained off. When bleaching-powder and hydrochloric acid are used, the former should be mixed to a paste with water. The fairly fluid paste is put through a cone mill to give it uniform consistency, stirred up with a large quantity of hot water in a strong petroleum barrel, and left to stand at least thirty-six to forty-eight hours. After this time a greenish-yellow coloured liquid is obtained, containing the effective ingredients of the bleaching-powder, this liquid is decanted from the lime sediment, which is thrown away as useless. The white precipitate of ferrous ferrocyanide is treated with a large quantity of hydrochloric acid, and the chlorine liquor is stirred in until a distinct smell of free chlorine is observable. The oxidation (blueing) takes place readily in the cold, but is accelerated by heating, with steam, to 70° to 80° C. The progress of the reaction is ascertained by taking samples from time to time. If the colour obtained with the original quantity of hydrochloric acid is not bright enough a further quantity is added, followed by a corresponding quantity of the chlorine liquor, and so on, until it is certain that the brightest possible shade of blue has been obtained. The colour must be finally washed in the usual manner and treated in other respects like all other brands of Prussian blue.

The oxidation of the white paste with aqua regia * is performed in exactly the same way. In this case, too, the results will be the better the stronger the consistency of the ferrous ferrocyanide. The white precipitate, therefore, should be filtered before oxidation with aqua regia, or pressed in the manner already described. In this case a mixture of acids consisting of 3 parts of hydrochloric acid (21° B.) and 1 part of nitric acid (40° B.) is used, and allowed to act on the white paste at a temperature of 70° to 80° C. When the oxidation is complete the blue colour is washed with hot water until the last washings are found to be perfectly free from acid.

Very handsome Prussian blues with a reddish tinge are obtained by oxidising the thin white paste with potassium chlorate and hydrochloric acid. To each 100 parts of potassium ferrocyanide about 12 parts of potassium chlorate and 25 of hydrochloric acid of sp. gr. 1·50 are required. In this case, too, the oxidation begins at once, but will not be complete until the mixture has been boiled for at least twenty minutes. The weighed quantity of hydrochloric acid is first added to the white precipitate, heated to about 60° C., the hot solution of potassium chlorate (12 : 100 water) being added immediately and well stirred in, the stirring being continued about fifteen to twenty minutes. After the oxidation is complete the mixture is allowed to stand twenty-four to thirty-six hours, and is then washed, filtered, pressed, and dried.

5. *Oxidation with Potassium Bichromate and Sulphuric Acid*

This method, which at the present prices of chrome salts is a relatively cheap one, can be recommended on account of its simplicity and perfect safety, especially to those making small quantities of Prussian blue for their own use. First the prescribed quantity of sulphuric acid is added to the white paste, heated to boiling. Then a hot solution of potassium bichromate is poured in, with continued stirring. The quantity of ferrous ferrocyanide obtained from 90 parts of ferrous sulphate and 100 parts of potassium ferrocyanide requires for its complete oxidation about 21 parts of potassium bichromate and 48 parts of concentrated sulphuric acid (66° B.). The oxidised product is allowed to stand twenty-four hours, and is then washed, filtered, pressed, and dried.

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* This process is no longer in use.

In all circumstances Prussian blue has always the same composition, whatever the method of oxidation employed, and it is asserted by some authorities that the same satisfactory results are obtained by using atmospheric oxygen as the oxidising agent instead of artificial means, assuming sufficient space and time to be at disposal. For this purpose the white paste is spread in thin layers on boards and exposed to the air until it has become deep blue throughout, *i.e.*, is completely oxidised, the operation being facilitated by wetting and turning the mass. For various reasons, however, this method cannot be adopted in practice.

The paler grades of commercial Prussian blue are called *steel blue*,* or *Milori blue* (*Chinese blue*). They are chiefly used in producing mixed green colours, especially the so called zinc green, a mixture of chemically pure zinc yellow, barytes, and Chinese blue. Only very few reliable particulars are really known about the manufacture of Chinese blue, the process being one of the small number that the manufacturers are still able to keep secret. On this account the production of first-class Chinese blue is restricted to a few makers. It is erroneous to assume that Chinese blue can be obtained by using smaller quantities of the oxidising agents, *i.e.*, by an incomplete oxidation of the white paste, since all the products obtained in this manner, even though much paler than the true Prussian blue, exhibit a greenish tinge, whereas perfect Chinese blue always has a decidedly reddish tinge which is highly valued by consumers. The analysis of this steel blue always reveals a certain amount of tin oxide, which seems to be essential to the production of the reddish tinge, even though it be assumed that the addition of tin salt to the solution of iron salt is merely with the object of reducing any ferric salt that may be present. The following method will furnish a bright Chinese blue (red tinge) in light and dark shades, as generally met with in commerce.

In this process ferrous chloride ($FeCl_2$) is used as raw material, prepared by dissolving iron filings in commercial hydrochloric acid, unless preference be given to the commercial chloride. To make the darker brand of Chinese blue 100 parts of potassium ferrocyanide are dissolved in 1200 parts of hot water. To this solution 25 parts of hydrochloric acid (21° B.) are added, and then heated to boiling by introducing direct steam. This temperature is maintained for half an hour, 65 parts of ferrous chloride ($FeCl_2$) being meanwhile dissolved separately in 650 parts of boiling water. The solution is treated with 1½ to 2 parts of tin salt, and then precipitated with the boiling hot solution of potassium ferrocyanide, the liquor being kept in continual motion by vigorous stirring. The white precipitate of ferrous ferrocyanide having settled down sufficiently—which will take two to three days—the perfectly clear solution is drawn off as completely as possible, and the white paste is oxidised by means of potassium chlorate and hydrochloric acid, at boiling temperature. The mass is washed with cold, soft water until the last washings are perfectly neutral.

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* Another and easier way to discriminate the various brands of Prussian blue is to apply the name *steel blue* to those devoid of the metallic lustre, and *bronze blue* to all kinds of Prussian blue (whatever their shades) which exhibit this remarkable metallic sheen.—*Translator.*

The lighter shade is obtained with the same quantities of raw materials by dissolving the potassium ferrocyanide and hydrochloric acid, ferrous chloride and tin salt separately (in boiling water) in two small tanks placed side by side above the precipitation tank. Both solutions are run at the same time into the working tank, which is half full of boiling water. The united solutions must be boiled thirty minutes, with constant stirring. The further treatment of the white paste is the same as already described.

These two brands of Chinese blue are very bright and soft in shade, with a distinct tinge of red. The pigment, cut into oblong pieces, is very light and delicate in texture—qualities that are unobtainable by other means. On precipitating ferrous sulphate with potassium ferricyanide, K_3FeCy_6, in suitable proportions, a dark blue precipitate is obtained. Formerly this was put on the market in a washed and dried state under the name *Turnbull's blue*, but is no longer used. At one time this colour was supposed to be a compound of different composition from Prussian blue, viz., Fe_5Cy_{12}; but it is now considered to be identical with pure Prussian blue, containing free potassium ferrocyanide, probably in accordance with the following equation:

$$\underbrace{4K_3FeCy_6}_{\text{Potassium ferricyanide}} + \underbrace{4FeSO_4}_{\text{Ferrous sulphate}} = \underbrace{Fe_7Cy_{18}}_{\text{Prussian blue}}$$

$$+ \underbrace{K_4FeCy_6}_{\text{Potassium ferrocyanide}} + \underbrace{4K_2SO_4}_{\text{Potassium sulphate.}}$$

Turnbull's blue is greatly inferior to Prussian blue in many respects, although it was formerly sold at a considerably higher price—a circumstance explaining its almost entire disappearance from the market.

It is an agreeable sign of progress in colour making that the innumerable cheaper brands of Prussian blue put on the market some time back under different names, such as mineral blue, Hamburg blue, new blue, Erlangen blue, &c., which owed their existence solely to very faulty and primitive methods of production, are now neglected by consumers, and are theref rightly falling into oblivion. The method of production was based on the use of impure prussiate solutions, containing variable quantities of potassium carbonate in addition to the pure ferrocyanide, precipitated with alumina, magnesium salts, zinc sulphate, &c. For this purpose the ferrous sulphate for the precipitation process was mixed with the above bodies, which in turn formed with the excess of potassium carbonate white precipitates mechanically incorporated with the Prussian blue. The oxidation of ferrous ferrocyanide was then effected simply by the influence of the air. At present less expensive adjuncts are mixed with the pure Prussian blue in order to obtain cheaper brands, which nevertheless are far more beautiful and more useful in practice than the former varieties of Prussian blue mentioned above, which were of very insignificant appearance owing to faulty methods of production. These additions include more especially starch, barytes, gypsum, raw and burned clay, &c., incorporated in a dry or pasty condition with the washed and filtered Prussian blue paste in variable quantities, according to the intended price of the product, the whole being finally ground repeatedly to obtain a uniform mixture.

Prussian blue was discovered in 1704 by Diesbach and Dippel, at Berlin, so that its German name, *Paris blue*, is incorrect. In France and England, however, it is more accurately called *Berlin blue* or *Prussian blue* (*bronze* and *Chinese blue*).

Direct Method

As already mentioned, only a few Prussian blues are made by direct precipitation of soluble ferric salts with potassium ferrocyanide, and these are much inferior in brightness to those produced by the indirect method. The difference with regard to the characteristic metallic copperlike lustre is especially striking, the latter exhibiting this feature in a higher degree, whilst the others are deficient in this respect, although generally brighter in shade. In the wet state the colour inclines more to violet, but changes on drying to a very full dark blue, lacking in brightness, a quality which the other products do not lose even when precipitated from very dilute solutions.

The ferric salts used in the manufacture of these so-called "*neutral*" *Prussian blues* are restricted to ferric sulphate, $Fe_2(SO_4)_3$, and ferric chloride, Fe_2Cl_6. The fact that both salts decompose very easily in a dilute state or at higher temperatures necessitates their use in a highly concentrated form, which is considered to account for the formation of very voluminous precipitates, and consequently their deficiency in respect of the coppery metallic lustre. Ferric chloride gives relatively brighter coloured precipitates than ferric sulphate, though both are characterised by containing an excess of potassium ferrocyanide, which cannot be removed by washing. The following method furnishes good results:

50 parts of ferric chloride are dissolved in a small tank placed above the precipitating tank, and charged with 200 parts of hot water at 60° C. At the same time 50 parts of potassium ferrocyanide are dissolved by boiling in a similar tank close by, and charged with 500 parts of water, 10 to 15 parts of hydrochloric acid (21° B.) being stirred into the solution. The precipitating tank is filled half full with water, heated to 60° to 70° C. by direct steam. This temperature being attained, the above chloride and ferrocyanide solutions are run in with vigorous and continued stirring, which is kept up without interruption for about twenty to thirty minutes after the last portion of the ferrocyanide solution has been added. The colour is then allowed to settle down, washed four to five times with hot water, filtered, pressed, and dried in the usual way.

Neutral Prussian blue may be mixed with the same adjuncts as that obtained by the indirect process.

Spent lime and sawdust from gasworks may be used as a raw material in the manufacture of Prussian blue. The mass contains ferrous sulphate or bog iron ore, the purpose of which is to purify the gas by removing the ammonia, sulphur, and cyanogen compounds present in crude coal gas.

To recover potassium ferrocyanide from these spent masses the ammonia compounds must be removed by leaching with water, and the sulphur extracted by carbon bisulphide. Caustic lime is next added, to dissociate the insoluble ferrocyanogen compounds, the dry mixture being heated to 80° to 100° C., and stirred, whereupon ammonia is liberated from a state of insoluble combination. Potassium ferrocyanide is leached out of the mass with water, and the solution is concentrated in presence of potassium chloride, whereby potassium calcium ferrocyanide, CaK_2FeCy_6, is obtained. The precipitated double cyanide is converted into prussiate by boiling with potassium carbonate.

Prussian blue can be obtained indirectly by precipitating the aforesaid solutions of calcium ferrocyanide in the usual manner with ferrous salts and oxidising the precipitate.

The cyanogen content is a criterion of the value of gas-lime, which is a much appreciated by-product.

Soluble Prussian Blue

For the manufacture of soluble Prussian blue *Brücke* gives the following recipe: A solution containing 271 parts of potassium ferrocyanide per 1000 is mixed with twice its volume of a cold saturated solution of Glauber salt. A second mixture is made of a similar solution of Glauber salt with a solution containing 100 parts of solid ferric chloride per 1000. Equal volumes of these two solutions are mixed and well stirred. The precipitate is allowed to settle down, filtered, and washed, until the washing water runs away blue. The colour is then dried at the ordinary temperature.

The capacity of oxalic acid for dissolving Prussian blue in a certain proportion affords a further means for converting this insoluble colour into such a condition that it will readily dissolve in all proportions of pure water that is free from lime. The operation is performed as follows: Pure Prussian blue in paste is thoroughly mixed with crystallised oxalic acid in the proportion of 10 parts of (dry) Prussian blue to 1 of oxalic acid. After a certain time the mixture becomes very fluid, solution being completed by thorough mixing and grinding in an ordinary cone mill. The thin paste is next placed in a tank of moderate size, and vigorously stirred with hot water. This treatment produces a bright blue ink-like liquid, which must be stirred up with a fairly concentrated solution of Glauber salt, to precipitate the soluble Prussian blue. In this way all the Prussian blue is reprecipitated as a voluminous curdy mass without losing its soluble character. The solubility, temporarily destroyed by the presence of Glauber salt, is restored on the removal of the latter. The precipitate is allowed to settle down thoroughly, the clear supernatant liquor removed completely, and the dark blue paste transferred to a filter, where it is drained and then washed with pure cold water until the washings exhibit a blue stain. This indicates that all the Glauber salt has been removed, and that the solubility of the Prussian blue is restored. The mass is afterwards pressed, cut into small oblong pieces, and dried at a moderate temperature (40° to 50° C.).

According to other recipes, Prussian blue is first treated for one to two days with hydrochloric acid or concentrated sulphuric acid, then washed, dried, and redissolved in oxalic acid. A stable solution is obtained by dissolving 8 parts of Prussian blue (treated with sulphuric acid) and 1 part of oxalic acid in 256 parts of water.

On pouring a solution of ferric chloride into an excess of potassium ferrocyanide solution, or, conversely, a solution of some ferrous salt of potassium ferricyanide, a deep blue precipitate is formed, whicth alumina has the formula $Fe_2K_2(Fe_2Cy_{12})$. On washing this precipitate perfeced, and from salt it will dissolve very readily in pure water, but loses this faculty vther heated to about 100° C. It is precipitated from solution by salts and alcoline

Soluble Prussian blue was formerly used as blue ink, and at present is employed by anatomists for injecting preparations of tissues, veins, &c. [In certain countries, like Italy, there is still a considerable demand for soluble blue.—*Translator.*]

Prussian blue is, strictly speaking, a glaze pigment, but of such intensity and colouring power that, in a concentrated state, it acts as a covering pigment. *Pohl* discovered that Prussian blue, especially in paste form, has been put on the market in admixture with starch, stained blue with iodine.

Prussian blue is decomposed on treatment with strong alkalies, concentrated acids, or by heat, but is more or less stable in presence of dilute acids and alkalies. On decomposing it with alkalies, brown ferric oxide is precipitated, and potassium ferrocyanide is re-formed in the solution. From this filtered alkaline solution Prussian blue can be reprecipitated, after acidification with hydrochloric acid, by adding ferric chloride. Prussian blue decomposed and oxidised by calcination in the air is used as a pigment by artists, under the name *Berlin brown.*

Prussian blue as an oil or water colour fades a little under the influence of air and light, especially the paler grades or light paints, obtained by mixing with white pigments. On removal from the influence of light and air for some time, and being kept in the dark, the faded colour will be restored to its pristine strength, a phenomenon which has not yet been satisfactorily explained.

Antwerp blue is a mixture of iron and zinc cyanogen compounds. It is prepared by mixing variable quantities of iron and zinc sulphates in solution, and precipitating them with potassium ferrocyanide.

c. Ultramarine (*Ultramarinblau, Bleu d'Outremer*).

The term "ultramarine" was originally used for a deep blue pigment obtained in the early middle ages, by a very complicated process, from lapis lazuli, a semi-precious stone that is still greatly appreciated. This mineral was mechanically ground, mixed with a special lute, and afterwards wrapped in cloths and kneaded for a long time under water, the fine blue colouring matter being thereby extracted from the mass and disseminated in the water, from which it gradually settled down. Repeated levigation and trituration gave a pure blue pigment that is stated to have been worth its weight in gold.

The chemical composition of natural ultramarine was first ascertained by *Désormes* and *Clément*, in 1806. They found :

Silica	35·8	per cent.
Alumina	34·8	„
Soda	23·2	„
Sulphur	3·1	„
Calcium carbonate	3·1	„
	100·0	„

irst and second decades of the past century several manufac-ermann at Schönebeck, *Kuhlmann* at Lille, *Tessaërt* at St. Gobain) d blue masses resembling ultramarine in the soda furnaces. *Klaproth*, especially *Vauquelin*, investigated this material, and found that its ehaviour toward reagents was very similar to ultramarine, its chief components being sulphur, silica, alumina, and sodium. In 1824 "the Société d'Encouragement" at Paris offered a prize of 6000 frs. for a method of producing ultramarine artificially, provided the cost did not exceed 300 frs. per kilogramme. *Guimet*, of Toulouse, was awarded this prize in 1828, being the first to devise a suitable process, whilst contemporaneously *Gmelin*, of Tübingen, published the same results. A process, perfected by *Köttig*, for producing artificial ultramarine was already in use at the Royal Porcelain Manufactory at Meissen in 1828, and this famous factory must therefore be considered as the birthplace of the German ultramarine industry.

The great bulk of the ultramarine now used is made in Germany and France. There, are, however, a few works in England, and also in the United States of America.

The sole ultramarines used for technical purposes are the sodium sulphur ultramarine, which can be obtained as white, green, blue, violet, red, and yellow pigments—one being convertible into the other by suitable treatment—of which, however, only the blue and perhaps also the green modifications are made on a large scale. The other existing potassium, lithium, silver, sulphur, and organic ultramarine compounds need not be described here.

Pure commercial ultramarine is an almost impalpable powder of a very bright azure blue and low specific gravity. It is absolutely insoluble in water, and unaltered by alkaline liquids, though very easily affected by dilute acids and even concentrated acid salts, which liberate hydrogen sulphide, and finally decolorise the ultramarine completely. Even concentrated solutions of alum can produce this result. The commercial "acid-proof ultramarine" is a product whose power of resisting the action of alum has been increased by an excess of silica.

The technical applications of ultramarine are very extensive. It is used for painting in oil, as well as in lime washes, for wall and fancy papers, for cloth printing, by litho and letterpress printers, in water-glass painting, &c. Materials of a yellowish or reddish white, or even dirty yellow, shade appear to the eye considerably whiter when mixed with small quantities of ultramarine blue, and important use is made in practice of this property. Thus, ultramarine is used for blueing linen, chalk and lime for whitewash, paper pulp, soap, starch, barytes, many fats, and even sugar.

There are three chief kinds of ultramarine blue in commerce, viz.:

1. *Glauber salt* or *sulphate ultramarine,* of a greenish tinge, is the palest of all brands of ultramarine. It has only a small covering power, and is the most readily affected by solutions of alum.

2. *Soda ultramarine low in sulphur,* of a pure blue shade, is much darker than the preceding kind, covers better, and offers more resistance to alum.

3. *Soda ultramarine rich in sulphur* is the darkest brand of all; it has a reddish tinge and high covering power. In consequence of its high silica content (besides sulphur) it has the greatest power of resisting alum, and is therefore preferred above all other sorts for blueing the pulp in paper-making.

Ultramarine is formed whenever sodium sulphide is calcined with alumina and silica in certain quantities. A green compound is first produced, and this, on further calcination, coupled with the influence of air and certain other ingredients, is converted into the blue modification—the true ultramarine blue. In practice, however, sodium sulphide is not employed direct, but is formed during the calcining process by the reduction of sodium sulphate with carbon, the necessary alumina and silica being applied in the form of china clay, which is an aluminium silicate, and therefore contains both these ingredients. Bearing in mind the brands containing sulphur and silica, the following raw materials are used in the manufacture of ultramarine:

1. China clay, or clays of similar composition.
2. Calcined soda (anhydrous).
3. Glauber salt (sodium sulphate), anhydrous.
4. Sulphur.
5. Carbon (charcoal, seldom pit coal), pitch, colophony, &c.
6. Silica in any suitable form.

Lampblack or similar bodies may be taken instead of coal, their fineness facilitating more intimate mixture and slower combustion, and therefore giving a more powerful reducing effect. Resin can only partly replace carbon, and, owing to its tendency to volatilise without decomposition, requires especial care, the operation having to be performed in tightly closed vessels. The qualities exacted of the said materials to render them suitable for the manufacture of ultramarine may be now briefly discussed.

1. *China Clay.*—In addition to English china clay, German (Amberg earth), Bohemian, and French pottery clays are used, of varying purity, and therefore always needing levigation. In all cases the china clay must be very finely pulverised, free from any excessive amount of oxides of iron or manganese, and as far as possible of uniform composition and physical condition. The composition, even from the same levigating works, being highly variable, the china clay must be analysed before use to enable a uniform ultramarine product to be obtained. The above-mentioned kinds of china clay contain the following average proportion of alumina and silica in 100 parts:

China clay . .	Alumina (Al_2O_3)	47	and silica (SiO_2)	53
Amberg earth . .	„ „	39	„ „	61
Bohemian china clay	„ „	42	„ „	58
French china clay .	„ „	44	„ „	56

2. *Calcined Soda.*—High-grade well-calcined soda alone should be used. The presence of 2 per cent. of sodium chloride will not be disadvantageous, but a high degree of moisture being unsuitable, the stock of soda should always be kept in dry storage places.

3. *Glauber salt,* or sodium sulphate, must also be well calcined, and as free as possible from acid. The content of sodium chloride should be the same as mentioned in the case of soda. Sodium sulphate should be free from acid or other impurities (lead, iron, &c.), and must be finely pulverised before use, preferably in stone edge-runner mills, to keep the salt out of contact with iron.

4. *Sulphur.*—Rod or stick sulphur is generally used. If it leaves only a blackish residue when volatilised in a small porcelain dish, the sulphur will

be suitable for manufacturing ultramarine; but cheap kinds of sulphur, which leave much residue on volatilisation, should be avoided, since they always produce dirty shades of colour. The sulphur should be pulverised as finely as possible in edge-runner or ball mills.

5. *Carbon.*—Charcoal made from pine trunks free from bark and knots is preferred. The content of moisture should not exceed 4 per cent. The charcoal must be pulverised in ball mills, and the resulting powder stored in a dry place. Only good-class pit coal can be used, free from sand, stones, and pyrites. The coal is pulverised first by edge-runners, and afterwards in ball mills. Charcoal has latterly been replaced in ultramarine works by other materials rich in carbon, such as resinous substances, colophony, black pitch, tar, asphaltum, &c. Colophony may be brown, but not contaminated with impurities.

6. *Kieselguhr* (diatomaceous earth) and *quartz* are used in the manufacture of siliceous varieties of ultramarine—*i.e.*, the darkest shades. These materials also must be used in a very finely pulverised state. The cheap calcined diatomaceous earth now on the market fulfils nearly all the conditions for manufacturing ultramarine, and is therefore very frequently used, although its bulky nature renders the mixture very loose. If quartz be used it must be very pure (washed), heated to redness, and afterwards thrown into water, whereupon it falls to pieces. When dry it is ground in edge-runners or large ball mills to a fine powder. Used by itself, quartz gives very handsome shades, somewhat paler than those furnished by the use of diatomaceous earth. Mixtures of these two substances are also employed.

According to a process patented by *Cross*, of London, coal and silica can be replaced altogether or partly by siliceous carbon, such as charred rice husks.

The manufacture of ultramarine blue is conducted in the following different stages:

1. Preparing the mixtures.
2. Calcining these mixtures (calcination product = green ultramarine).
3. Crushing the green ultramarine.
4. Blueing of the green ultramarine by roasting (fine burning).
5. Lixiviating (washing) the roasted product, wet-grinding, levigating, pressing, and drying.
6. Sifting (bolting) the dried products.

1. *Preparing the Mixtures*

A very important factor in the manufacture of ultramarine is the choice of suitable proportions in mixing the raw materials; but considerable divergence of opinion prevails on this point, especially with reference to the larger or smaller excess of the sodium salt in the mixture. *Unger* gives the proportions of china clay and sodium salt as 1 : 6. *Buchner* and *Fürstenau*, however, took the proportion 1 : 3, 2 : 4, and afterwards even 2 : 3 as giving the best results. According to experience, any reduction below this latter proportion will considerably lessen the brightness of the resulting ultramarine, so that this is apparently the utmost limit practicable. The following mixtures are said to be the best, provided faultless raw materials are employed:

Ultramarine Blue.	Pale.	Medium.	Dark.
China clay	100	100	100
Soda	9	100	103
Glauber salt	120	—	--
Carbon	25	12	4
Kieselguhr (diatomaceous earth)	—	—	16
Sulphur	16	60	117

The products obtained from these proportions may be considered typical of the three grades of ultramarine, the other (intermediate) shades being obtainable therefrom by mixing. The addition of diatomaceous earth depends on the amount of alumina in the china clay, and must therefore always be calculated from the composition of the china clay used.

100 parts $Al_2Si_2O_7$ contain 53·9 SiO_2 and 46·10 Al_2O_3.
100 „ $Al_2Si_3O_9$ „ 63·7 „ 36·3 „

The mixing of the weighed raw materials in the above proportions can be performed in different ways. The most intimate and at the same time cheapest mixture is obtained when the raw materials have been worked, first of all in edge-runner mills, and afterwards ground very fine in ordinary balance-mills. The grinding in the edge-runner mill must be continued so long as any fragments of carbon can be detected in the resulting powder. The latter must be perfectly homogeneous and free from stripes of different colours when spread out with a steel or horn spatula. The mixtures containing much sulphur must be ground to a fine, homogeneous powder first, and reground two or three times after the suitable quantity of sulphur has been added. The finished mixtures must not be left to stand, but should be worked up at once.

2. *Calcining Ultramarine Mixtures. Green Ultramarine*

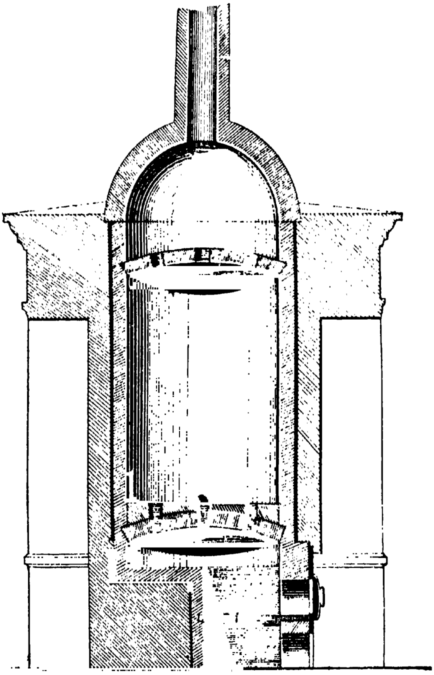
This operation is performed in cylindrical or tapered fireclay crucibles, placed one upon another in a kind of muffle furnace similar to those used in porcelain works, and exposed to a temperature between red and white heat for seven to ten hours. The tapered crucibles are preferred to those of cylindrical shape, owing to the better circulation of heat even when they are packed closely together in the furnace. In many works up to seven layers of crucibles will be used, and the lids must therefore be strong enough for the lower ones to stand the pressure of the rest without damage. In large works several muffle furnaces will be arranged side by side, separated only by a strong wall, so that all the escaping gases are led into one chimney-stack. The construction of the furnaces should be as simple as possible. The shape is immaterial, the chief consideration being proper dimensions, and, above all, a suitable and easily regulated draught. This is the only way in which a proper temperature can be applied equally to all the crucibles, and thereby render a successful result possible. In no case should the dimensions of the furnace be larger than is required for accommodating crucibles containing an aggregate charge of 6 to 8 cwt. The furnaces are naturally of greater height than breadth, and of square (seldom round) section. The inside is lined with firebrick wherever the surface comes in direct contact with the heat. Ordinary coal, coke, peat, and wood may be used as fuel.

In filling the crucibles the raw materials must be pressed down somewhat (as far as can be done without loss), and the lids put on in such a way that they do not come in contact with the charge. They are then placed in the furnace, one by one, in rows and layers, the mouth of the furnace being loosely closed with fire-brick and the joints outside luted with soft clay. To enable the temperature in the furnace to be measured and the progress and completion of the reaction to be gauged, two loose bricks are inserted in different parts of the furnace mouth, and these can be taken out for watching the course of events inside. The duration of the calcination process depends on the ingredients and proportions of the mixture, the dimensions of the furnace, the draught, the fuel, and various other circumstances, so no definite instructions can be given on this point. Usually the duration of the reaction depends on the formation of the sodium sulphide, the length of the calcination process varying inversely with the amount of sodium sulphide in the product. This must be ascertained by preliminary trials.

When the reaction is finished the ash-pit holes must be bricked up, the loose bricks put into the inspection openings and luted, both these and all other openings through which air could enter being shut as tight as possible. The furnace is then left to cool down, which generally takes two to three days. As soon as the furnace is emptied it can be recharged at once.

For calcining larger quantities the so-called shaft furnaces are used, holding up to 2 tons of the crude mixture. These are large cylindrical furnaces, the fire-brick shaft being supported and protected by strong walls, of such a form as to secure equal distribution of the pressure exerted from the inside. Gradual bulging of the walls, especially at the charging hole, is thereby avoided. The cylindrical shaft is topped by a dome, similar to a cowl, either supporting the chimney or connected with the main factory stack by a flue. Immediately below the dome is a flat vault of fire-brick, forming the actual roof of the shaft. A number of round or rectangular openings in the vault allow the smoke and hot gases to escape into the space between the vault and the dome, and thence into the chimney. In this manner an equal distribution of heat is secured in all parts of the shaft. The furnace is arranged underneath a second vault, with a flattened top forming the floor or sole of the shaft. The heating gases pass through a great number of flues in the floor and enter the calcination chamber, filled with crucibles, arranged in layers, and after traversing this chamber in all directions they escape as mentioned above, through the dome of the furnace into the chimney. A suitable opening must, of course, be provided for cleaning the dome from time to time. These furnaces possess nearly all the advantages of the older type of furnace, and may be used for green calcination as well as for the direct blue calcination process, without the necessity for special repairs so frequent in the other type of furnace. At the same time they enable the heat of the fire to be equally distributed in the most perfect manner, thus facilitating considerably the otherwise difficult task of controlling the calcination process. Moreover, the working of this furnace does not depend on any special fuel, all kinds being equally suitable. Finally, as already mentioned, it will accommodate a far larger charge than the muffle furnace. Fig. 59 represents a sketch of a shaft furnace.

FIG. 59.



The calcination process of a Glauber salt mixture in the shaft furnace is the same as in the muffle furnace; but in the case of soda mixtures low in sulphur the heating of the shaft must be conducted in such a manner that a bright red heat is only attained after four to five hours. The heating process must therefore take at least nine hours. This is also the case with mixtures containing alum, except that the temperature must not exceed dark red heat.

The product obtained by calcining the raw mixture with exclusion of air is the green ultramarine, and is better in proportion as it is softer, and exhibits less of a blue tinge on the surface. When the green product is to be sold as such the blue particles must be carefully separated from the rest, but this is unnecessary when the mass is to be converted into blue. In both cases, however, care must be taken that the mass from the crucibles does not contain any uncalcined particles of the raw materials. The presence of these latter is indicated by the reddish-green appearance of the calcined product, and although it does not generally have any disturbing influence on the subsequent stages of the process, the particles being oxidised into the green modification on the admission of air, it would reduce the commercial value of the ultramarine green.

Curtius has made the calcination a continuous operation by his patented process. He uses a cast-iron retort, lined inside with fire-proof cement. The retort, similar to gas retorts, is set in brickwork, and is provided with receivers for condensing the sulphur vapour, as well as with flues for removing the gases. When charged, the retort is closed front and back, but air can be admitted from behind, thus enabling the green ultramarine formed in the retort to be quickly converted into ultramarine blue. The oxidising process can also be effected in a brick receptacle underneath, into which the finished green is easily discharged from the retort, leaving the latter free to be recharged at once.

3. *Grinding the Green Ultramarine*

Ultramarine green must be put through a special treatment before it can be converted into the blue modification by the finishing calcination in presence of sulphur. This treatment will vary according to the composition and physical character of the green ultramarine.

Although the quality of the blue product obtained by the finishing calcination primarily depends on that of the crude green ultramarine, the method of crushing the latter into the finely divided state most suitable for the blueing process has also a certain influence on the result. The brightness of the ultramarine blue depends largely on the brilliancy of the crude green product, and since this characteristic suffers in proportion to the pressure applied in grinding, it is obvious that care must be taken to avoid any unnecessary pressure in performing that operation.

The grinding of the crude green material is effected in two different stages—the crushing, which is the same for all kinds of green, and the subsequent grinding in dry mills, this latter operation varying according to the softness of the material.

The material is exclusively crushed in roller mills. These are fitted with deeply fluted or sharp-toothed iron rollers, which rotate close together without actually touching, so that the material, fed through a suitable hopper, is crushed between them and delivered into a wooden box underneath. In some works iron rollers are replaced by those of wood fitted with ribs of strong iron hoops instead of fluting or teeth. The crushed mass is in granules about the size of peas, which must be ground further, especially in the case of Glauber salt greens, owing to their excessive hardness militating against the success of the final roasting. This grinding is performed in dry mills, which can be adjusted so as to furnish a powder of any desired degree of fineness. The degree of grinding necessary for Glauber salt green for yielding a good blue product in the finishing calcination must be determined beforehand by experiments on a small scale, a certain amount of skill and practical experience being required. The roasting process will give better results in proportion as the green material has been more finely powdered, though beyond a certain point at the sacrifice of brightness in the resulting ultramarine blue.

The soda greens, generally much softer, will not in most cases bear the strong grinding usually required in the case of the Glauber salt greens, and, when crushed the application of heavy pressure in further grinding must be avoided as much as possible. Formerly the operation was performed in rolling casks, ten to twenty or more being revolved at a time, according to the size of the works. This method is still practised in many small establishments on account of its satisfactory results. The iron balls of different size in the revolving barrels gradually reduce the material to a fine powder, which is then passed through a fine sieve to separate the coarser particles. The barrels are arranged on a solid frame in two parallel rows, with their longitudinal axes in the direction of the narrow side of the frame. The rotary motion is imparted by a common shaft passing longitudinally through the middle of the frame, and transmitting movement to the barrels through cog-wheels, each barrel being fitted with a special stop-motion. The shape of these barrels should be oval rather than circular, and the charging holes must be closed by a dust-tight cover, held in place by a bow and screw in the usual manner, the joints being packed with felt, indiarubber, &c.

Revolving barrels, being clumsy and inconvenient, have been replaced by ball mills, fitted with sifting devices ensuring continuous working. When suitably constructed, these mills render the crushing of the raw green quite superfluous. For the same purpose cone mills and even pulverisers are used in many cases. The further treatment of the green ultramarine to purify it from the adherent saline impurities before blueing has been greatly improved. Whereas formerly the crude green had to be first ground in wet mills (like white lead mills) and then steamed until it could be levigated, this treatment is now abandoned entirely, and the green is usually ground dry (with the impurities) and roasted direct, this treatment giving equally good results, provided selected raw materials are used and the final calcination is carefully controlled. For the same reason the later process of lixiviating the ultramarine green after dry grinding is now confined to a few manufactories, and only when the green is to be sold as such.

4. *Colouring Ultramarine by Roasting*

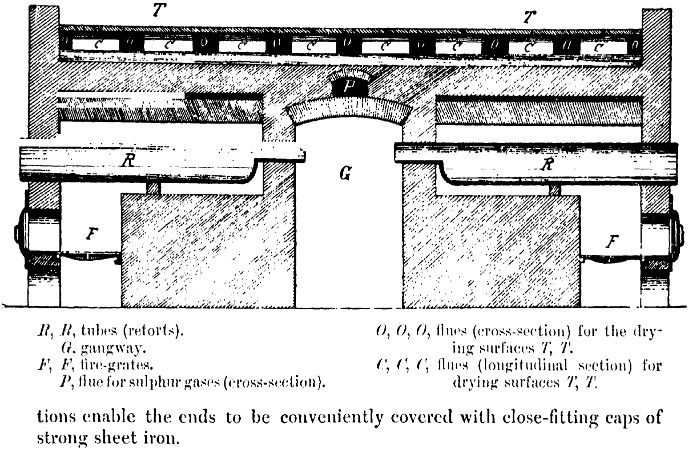
The roasting of the crude ultramarine green to convert it into the blue modification has undergone more changes than any other stage of the manufacturing process, as the result of constant search for improvement and simplification, though, of course, not always with the desired result. It is not our task to consider in this place all the proposals published in the technical literature in this connection, more especially since it is very difficult to ascertain whether any of these proposed improvements have actually found practical application. Leaving out of consideration the manufacture of ultramarines containing much silica, which are obtained direct from the mixtures of raw materials by a single calcination, no very great improvements can be found in relation to the construction of furnaces for the final roasting. What modifications there are refer mostly to increased dimensions; and really these furnaces seem to have as many opponents as friends. A short description of the furnace preferably used for this process will now be given.

In the oldest types of furnace for ultramarine blue roasting we find attempts made to utilise the waste heat of the primary calcination furnaces for the final roasting process. This was done in the simplest way by erecting above the calcining chamber a second arched floor, on the bed of which the crude green could be roasted. The fire gases were led either through suitable flues below the bed, or admitted direct into the roasting chamber. Since in this arrangement the final roasting depended on the duration of the calcination process, it was subjected to frequent interruptions, which, although not unfavourably influencing the appearance of the blue, delayed the whole process in an undesirable manner. Special furnaces were therefore constructed for the roasting process, and of these the muffle and retort furnaces seem to have answered best, since they are still used in all ultramarine works.

The *cylindrical* or *retort furnaces* (Fig. 60) consist of an arrangement of strong cast-iron tubes, each 16 ins. in diameter and 80 ins. in length, generally built into the furnaces in sets of three, so that the flame laps them on all sides.

The tubes project at the front end next the fire-grate, as well as at the rear end of the furnaces, about 2 ins. beyond the brickwork. These projections enable the ends to be conveniently covered with close-fitting caps of strong sheet iron.

FIG. 60.



R, *R*, tubes (retorts).
G, gangway.
F, *F*, fire-grates.
P, flue for sulphur gases (cross-section).
O, *O*, *O*, flues (cross-section) for the drying surfaces *T*, *T*.
C, *C*, *C*, flues (longitudinal section) for drying surfaces *T*, *T*.

Two different kinds of caps are in use, some covering the ends of the tubes completely, others leaving them about one-quarter open. The latter shape is put on during the converting process. In large works, where a number of cylindrical furnaces are in work at the same time, they are mounted in pairs back to back, with an intervening space about 16 to 20 ins. across. A small passage is thus left between them, and this is covered with an arched roof, its length increasing with the number of furnaces composing the battery. All the flues or pipes from the various furnaces discharge into this passage, which, being closed at both ends by doors, and connected directly with the main chimney-stack, forms a flue, with a strong draught to carry off the large volumes of poisonous gases containing sulphur, &c., given off in the process, and prevent any inconvenience on this account to the men working at the front end of the furnaces. The passage communicates with the chimney-stack by means of a flue built along the roof of the passage itself, which flue is connected with the passage by openings (about 12 by 10 ins.) in the roof of the passage midway between each pair of furnaces, and closed by iron slides. The most suitable arrangement of the furnaces is to set them up at right angles to the length of the building, so that the windows of the furnace room will throw sufficient light for the supervision of the work.

Neither the shape nor the foregoing arrangement of the cylinder furnaces has undergone much change in course of time except as regards the retorts. Those formerly used were very small (6 to 7 ins.) in diameter, and very seldom exceeded 5 ft. in length. The larger dimensions given above as now being used appear to have reached the limits of practicability, any further increase being probably the reverse of beneficial. For instance, larger retorts would increase the difficulty of manipulating the charge, and at the same time the greater free space above the charge would cause a considerable loss of heat, and thereby increase the consumption of fuel. To facilitate the burning of the charge, and exposing fresh surfaces to the action of sulphur dioxide, agitators have been proposed, consisting of rotary vanes mounted on a horizontal shaft, so as to scrape the sides of the retort on the shaft being turned. These, however, did not act perfectly, the colour usually burning on the walls of the retort, and either remaining green or turning quite white. This circumstance may have been the principal reason why this arrangement—which is apparently a desirable one—has gone out of use, and is at present found only in a few works.

Muffle furnaces (Fig. 61) are preferred in many large works. Their construction is very simple, and the various kinds only differ in points of detail. The muffle, either made of fire-clay throughout or with fire-clay sides and an iron top, is built into the furnace. The sole or hearth forms the cover of the heating chamber, the flame passing upwards through a number of flues provided on both sides in the walls of the muffle and over the arched top into the chimney. The hearth is made of strong fire-clay plates with lap joints, luted or cemented together, and the whole surface smoothed before using. The muffle, when wholly or partly of iron, projects about two inches from the sides of the furnace to enable it to be tightly closed with the iron lid, which must be luted all round. Muffles made of fire-clay throughout should be built in completely at the back and closed in front, except for a semicircular hole, the base of which coincides with the surface of the hearth. Through this hole the muffle is charged and emptied, and the opening may be closed, if required, by a counterpoised iron slide working easily in an iron frame. The opening is arched over with a hood, for conveying the gases into the chimney, since the sulphurous fume escapes through the working door and has to be regulated by the slide.

The dimensions of the muffle furnaces are not, like those of the cylinder furnaces, restricted within certain limits, and therefore muffle furnaces of very different sizes are found in practice. It must not, however, be concluded that large muffle furnaces are more profitable than the smaller retort furnaces, for whilst in the latter the heating of the crude green can easily be finished in one day (without a night shift), the heating process in the muffle furnaces takes (with day and night shifts) three to six days, according to the dimensions of the muffles. Considering further the fact that the mixing of the charge is effected far more quickly and thoroughly in the cylindrical furnaces, whilst the discharge of the superfluous sulphur fumes is far more convenient and absolutely safe, the cylinder furnace is decidedly preferable. It cannot be ascertained whether any other furnaces are really used in ultramarine works. Other types have been proposed in the technical press, but it is not known to what extent they have found application.

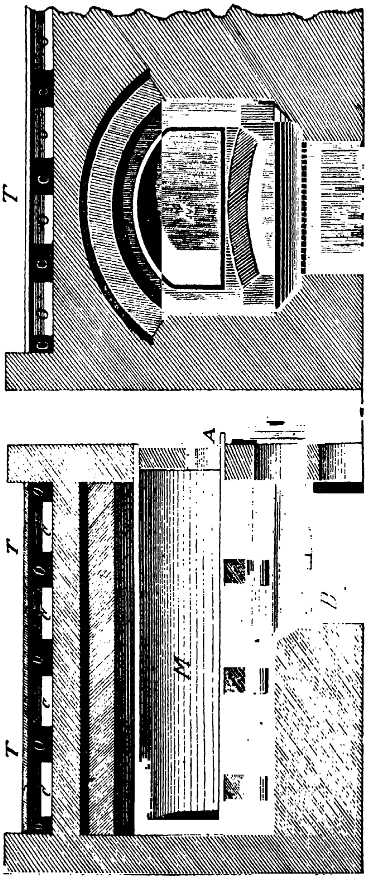


Fig. 61.

M, muffle.
B, ash-pit.
C, drying-flues (cross-section).
O, drying-flues (longitudinal section).
T, drying-surface.

M, muffle.
A, charging aperture.
B, ash-pit.
T, drying surface.
C, flues (longitudinal section).
O, flues (cross-section).

The *blueing* of the ultramarine green on the large scale is effected, as already mentioned, by heating with sulphur. In comparison with certain other materials, such as sal ammoniac, hydrochloric acid, boric acid, chlorine, &c.,

which are also able to produce the colour change under certain conditions, the application of sulphur has the advantage of performing this change in a relatively very short time.

When green ultramarine is heated the admixed sulphur burns to sulphur dioxide, a part of the sodium contained in the ultramarine green being also oxidised to sodium sulphate. This can be detected in the washing from the resulting blue. Hence a loss of sodium is incurred in the formation of ultramarine, and a similar loss occurs through all the states of the ultramarine process. In the formation of **green ultramarine** of the formula $Si_6Al_6Na_8S_2O_{24}$ the five molecules of Na_2SO_4 are reduced by the heated carbon to $5Na_2SO_3$, of which, as the temperature increases, four molecules will be decomposed to three molecules of $Na_2SO_4 + Na_2S$. The resulting three molecules of Na_2SO_4 are again reduced by the carbon to $3Na_2SO_3$ and decompose again, with the remaining fifth molecule of Na_2SO_3, to $3Na_2SO_4$ and Na_2S. Therefore at a certain stage of the heating process there will be three molecules of Na_2SO_4 besides two molecules of Na_2S. Finally, at a higher temperature the silica also enters into the reaction, and, since the presence of the carbon makes the conditions favourable, deprives the Na_2SO_4 of the Na_2O, the nucleus $Si_6Al_6O_{24}$ being formed. The two free affinities of this, when saturated by 2NaS, give the compound $Si_6Al_6Na_8S_2O_{24}$, **green ultramarine** ($Si_6Al_6Na_6O_{24} + 2NaS = Si_6Al_6Na_8S_2O_{24}$). The 2NaS entering into the nucleus must be assumed to have resulted by the influence of the sulphurous acid liberated from the sodium sulphate by the combination of the Na_2O with the silica.

Exactly the same process takes place at the beginning of the heating process. The sulphurous acid liberated from the green ultramarine abstracts sodium by forming sodium sulphate, whereby the quantity of sulphur in the ultramarine blue will increase in comparison to that present in the green (crude green contains three-fifths, crude blue four-fifths of sulphur). One-fifth of the sulphur escapes partly as sulphurous acid, partly uncombined. That a loss of sodium does take place in the conversion of green ultramarine into blue can be proved by employing some other converting reagent, such as gaseous HCl, phosphoric acid, boric acid, chlorine, &c., in all of which cases, besides the blue, the formation of a soluble salt of sodium can be proved.

The *roasting process* itself is carried out in very different ways in practice. It depends, of course, primarily on the construction of the furnaces, but also, on the other hand, on the use of the necessary quantity of sulphur for colouring. With soda green this quantity is 7 per cent., and with Glauber salt green 9 to 10 per cent. of the weight of crude green, and must be either added before heating or supplied to the furnace gradually during the course of the heating process until the required intensity of the blue has been attained. The first method is worked as follows: Before the mixture of crude green and sulphur has been supplied to the cylinders or muffles these latter must be already in a glowing or strongly heated state, and the heat in the furnaces must correspond to that one in the colouring furnaces. According to the character of the crude green to be treated, the charging temperature will vary. The highest charging temperature—bright red heat—is required for Glauber salt green, while soda greens can be charged at a somewhat lower temperature, say medium red heat. When the crude green contains alum it must be roasted in muffles, heated until the hearth of the muffles has attained a low red heat. After the furnace has been charged the treatment is the same for all kinds of green, unless, as already mentioned, the construction of the furnaces requires some alteration of the working methods. Retort furnaces are charged with semicircular shovels, muffles with flat iron ones, the work being done as quickly as possible to avoid excessive cooling. Before this is done the full caps must be taken off the cylinder ends projecting into the gangway, and replaced by the three-quarter caps. When the charge is in the furnace it must be thoroughly well mixed and spread out flat to form an even layer. In retort furnaces the cap on the charging end is also replaced, the muffles being, however, closed by letting down the slides, but leaving a sufficient outlet for the sulphur gases. The mass in the muffle is mixed with copper rakes fastened on long iron rods. Similar rakes, but of a smaller size, can also be employed to mix the materials in the retorts, but for this purpose moderately thick round iron bars are generally used.

Immediately the furnaces have been charged, or a short time afterwards, the reaction begins under the influence of the increasing temperature. The sulphur melts and burns gradually, forming sulphurous acid (sulphur dioxide), which escapes in the form of white fumes. At the same time the green ultramarine shows a distinct alteration, the brightness increasing and the shade becoming darker.

The material having been exposed for about thirty minutes to the influence of the sulphur, the caps on the working end of the retorts must be taken off, and the contents of each cylinder mixed thoroughly and levelled down again. The same is done in the case of muffles. This operation must be repeated every half-hour, until the whole of the sulphur has been burned off. This will be indicated by the green colour of the charge gradually changing into blue, which does not occur until all the excess of sulphur has been consumed. Samples must then be taken each time the charge is turned, these being spread out in the usual manner with a spatula and examined for the presence of white specks in the mass. As soon as these appear the suitable temperature may be assumed to have been exceeded—a condition which must, if possible, be avoided. It is advisable to keep the temperature of the furnaces at the same level for about forty-five minutes to an hour after the sulphur is burned off, and then reducing the fire gradually, stopping it altogether after two and a half to three hours. During this period, too, the heated product must be turned over every thirty minutes. The caps must be replaced after each turning, the slides being returned to the proper position in the case of muffles.

It may be mentioned here that the unwashed, crude ultramarine green differs from the washed green in the course of the colouring process, owing to its tendency to ball. In such cases the charge needs a very careful turning, and any balls detected must be crushed with the iron rods in order to reduce the powder to the requisite fineness.

When the mass in the furnace has been cooled so far that a chip of wood thrown into the cylinders or muffles will no longer ignite, several vessels, each containing about a quart of water, must be inserted in each muffle (one in the case of retorts). The furnace must be closed by means of the caps (or slides, as the case may be), and the joints made air-tight by luting with clay (mixed with fire-clay, to prevent cracking), in order to exclude air completely. The furnaces are allowed to cool during the night, and are opened next morning, the still hot colour being emptied into iron boxes provided for this purpose. Here the colour is left until quite cold, which will take two to three days, according to the external temperature.

The other method of colouring, in which the necessary sulphur is supplied to the crude green ultramarine in successive portions, may be shortly described as follows: The cylinders, or muffles, being heated as described, must be charged with the crude ultramarine green, and the mass carefully levelled with a rake or iron rod. Each cylinder must be charged with about ½ cwt. of green (for sizes not less than 16 ins. in diameter), but the muffles with about 1½ cwt. of raw material each. The charge must be spread out on all sides to a uniform depth of 2½ to 3½ ins. To ascertain the precise moment for adding the first portion of sulphur a lump of sulphur must be thrown on the layer of charge when the latter is heated right through; if the sulphur ignites at once the first portion may be added. To prevent the temperature rising at this stage the fire should be drawn or moderated by suitable means. A portion of the sulphur is then shovelled in, stirred up uniformly with the charge, and left to burn away completely. This operation must be repeated until the green colour has changed to a bright blue, the end point being easily and accurately tested by taking out a small sample and spreading it with a steel spatula. In retort furnaces the portions of sulphur do not amount to more than 1½ lbs. at a time, about three times this quantity being used for the muffles. In other respects the working of the furnaces and the material is almost the same throughout as in the methods formerly described (*q.v.*).

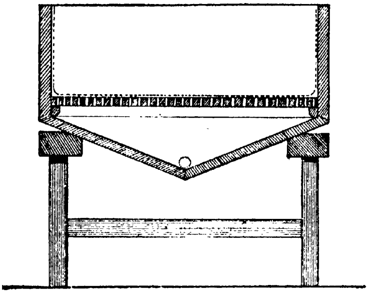
Ultramarine rich in silica which, as already mentioned, is a soda ultramarine, containing in the crude mixture up to 10 per cent. of finely ground silica (diatomaceous earth, &c.), based on the weight of china clay, does not require a supplementary treatment with sulphur, but is roasted in specially constructed furnaces direct from the crude mixture. For this purpose crucible furnaces, or furnaces in which the mixture is calcined in stone troughs, holding 5-ton charges at a time, are used. The stone troughs are 17 to 20 ft. long and 10 to 13 ft. wide, and are placed in the furnace in such a way that they can be reached on all sides by the flame. The mixture is placed in the troughs, spread out to a depth of 12 to 16 ins., covered with fire-bricks, and then calcined for about three weeks. By this process a very bright and brilliant ultramarine blue is obtained, and one that offers greater resistance to the influence of alum than any other kind of ultramarine. One defect of this product, however, is its high content of free sulphur, which renders it useless for certain purposes.

5. *Lixiviating and finishing the Ultramarine*

As has been seen in the explanation of the formative process of ultramarine blue, the impurities to be removed by lixiviation after calcination consist of a larger or smaller quantity of Glauber salt. The manner of effecting this operation is, however, by no means a matter of indifference, the quantities to be dealt with in large ultramarine works rendering the recovery of the Glauber salt a profitable affair. The solution must therefore be strong enough to enable it to be concentrated for crystallisation without any considerable expense. The numerous processes fulfilling this purpose more or less satisfactorily cannot all be described here, and we will confine ourselves to only one, which is largely used on account of its simplicity, and may therefore be regarded as typical.

The tanks in which the calcined material is lixiviated are simple filtering boxes of 1-in. to 1½-in. pine, measuring 5 to 7 ft. long and 40 to 60 ins. wide. A large number of such boxes will be required, arranged in rows in a room with a cemented or asphalted floor. Between each three to four boxes a wide gangway is left, to allow sufficient room for readily carrying out the work. The solid bottom of the boxes is either quite flat or sloping from the sides toward the middle (Fig. 62). About 6 to 8 ins. above the bottom is mounted a false bottom, resting upon ledges, and perforated with a large number of ¾-in. holes. This is the most important part of the whole apparatus, and is covered with a strong cotton cloth, forming the real filtering surface. This cloth is fastened inside the walls of the boxes at a height of ½ to 2 ins. from the false bottom with small nails driven in very close together, so as to make a tight joint all round and prevent the escape of even the finest particles of colour. Close above the true bottom at one end of the box (at the lowest point of the slope) is a hole about 1¼ ins. wide for drawing off the filtered Glauber salt solutions into a vessel underneath. This hole is closed with a wooden tap or a spigot. The boxes are arranged in threes on strong wooden frames. The method of lixiviating the ultramarine is as follows:

FIG. 62.



The cold, calcined material from the furnace can be lixiviated at once, for which purpose a portion of the ultramarine blue is suffused in a small vat with a little hot water (75° to 80° C.) and thoroughly mixed for some time, the resulting paste being sifted into the nearest filtering box. Should the paste be too stiff to rub through the sieve with a brush except with considerable loss of time, more water must be added to thin it down and accelerate the work. In this manner the filtering boxes are filled in succession until the stock of colour is exhausted. In large works, where seventy to eighty such boxes are used, a rail-track is laid between the rows, to convey a flat truck carrying the above-mentioned vat for charging the boxes.

The wet colour is left on the filters, whereupon the Glauber salt, in solution, trickles through the filtering cloth into the empty space between the false bottom and the real bottom of the box. If the perfectly clear solution has a density of 15° B. or more, it may be transferred immediately to cool rooms for crystallising. Weaker solutions, however, must first be concentrated in evaporating pans, which are flat, usually iron vessels, heated by the waste heat from the calcining or roasting furnaces.

After the first solution of Glauber salt has been removed from the boxes the draw-off plug is replaced, and hot water again poured on to the colour. The same process will be repeated, but this time a far weaker solution is obtained than before. The operation must be continued until the last trace of Glauber salt has been extracted from the ultramarine. With care, even a third solution suitable for concentration will usually be obtained, but the rest is so weak that this is no longer feasible, and unless it can be utilised in some other way (perhaps for manufacturing blanc fixe) it must be discharged into the drains.

Before the colour remaining in the filtering boxes can be treated further it must be tested to see if all the Glauber salt has actually been removed, barium chloride being used for this purpose. If on adding a few drops of this reagent to a test-tube half full of the clear filtrate a white precipitate is formed, the washings still contain Glauber salt—*i.e.*, the colour has not yet been thoroughly washed. On the other hand, if the solution remains clear after the addition of the barium chloride, or shows only a faint white cloudiness, the colour may be considered as pure and the process finished. In testing with barium chloride the nature of the water used must be taken into consideration, since water containing dissolved sulphates (mostly gypsum) by itself gives a white turbidity under this test. It is advisable, therefore, to acidify the test sample with pure hydrochloric acid.

The next stage in finishing the washed ultramarine blue consists of *wet grinding*. Formerly for this purpose mills similar to white-lead mills were used, but nowadays only the so-called wet mills are employed (see Fig. 9) as described on page 25. It may be mentioned that for this process the stones should run at a speed not exceeding eighteen to twenty revolutions per minute. The number of mills required will vary according to the size of the works. They are arranged in three to four terraces, or in rows side by side. In the former case the thin liquid colour is fed to the top mill, from which it runs down a gutter into the next one below, and so on, until it issues from the lowest one into a collecting tank. When the mills are placed side by side in rows each grinds a stated quantity of colour, so that the ground material can be drawn off from the mill direct into a collecting tank.

Since sodium silicate passes into solution in the wet grinding of ultramarine blue, it is therefore essential that soft water should be used for grinding. Water containing dissolved compounds of lime would precipitate the sodium silicate, forming calcium silicate, which retards the subsequent levigation of the colour. Hence for this operation, where steam is available—which will nearly always be the case—it is preferable to use condensed water, which can be obtained in sufficient quantity without any great expense.

The quantity of colour fed to each mill depends, of course, on the diameter of the stones. The success of the grinding process requires that stones of moderate size should be used, and therefore the weight of the material fed to each mill may be taken, on the average, as not more than 18 to 20 lbs. of dry colour. In many works the quantity is even less, viz., 9 to 10 lbs.

With regard to the duration of the grinding process, no definite particulars can be given, so much depending on the nature of the colour. For dark shades about two hours are sufficient, but light and high-class brands will take longer, apart from the consideration that under certain circumstances a second grinding may be required, though this is only the case when it seems probable that the levigation residue will pay for regrinding.

In setting the wet mills the stones should not be brought into actual grinding contact immediately on starting, but should be set closer and closer by degrees, the final position being attained in about an hour from the start.

To ascertain the progress of the grinding process samples must be drawn from time to time, by means of a small wooden rod, and placed on white filter paper, the drops being dried as quickly as possible. A lustrous surface indicates, as a rule, sufficient grinding. When an equally finely ground product has been obtained from all the mills the whole is delivered to the common collecting vessel, a large wooden vat, and allowed to stand for thirty-six to forty-eight hours.

The next operation separates the finer particles of the ground colour from the ever present harder particles, by a *levigating process*, which is highly important and requires much patience and attention.

The colour in the collecting tank deposits the bulk of the blue during the thirty-six to forty-eight hours aforesaid. The blue top liquor, containing the finest particles of colour in suspension, is baled into a vat and left there until the smallest particles of blue have settled down completely. This fine sediment will be afterwards mixed with the other products. Since ultramarine blue is one of those pigments which settle down very compactly on the bottom of the vessel when deposited from suspension in water, it is generally necessary to use an iron bar to loosen the colour sediment in the collecting tank. The dislodged paste, which is so stiff as to be easily crumbled, must be divided equally among a number of levigating tanks in such a manner that each tank, 40 ins. high inside and of the same diameter, receives about 2 cwt. of dry colour. The levigation tanks are filled three-fourths full with soft, preferably condensed water, and the pasty colour simply crumbled in, the whole being mixed until the colour is equally distributed through the water. The procedure is exactly the same with all the tanks used for washing and levigating the stock of colour. This washing is for the purpose of separating the coarse particles from the finer ones, the former now settling down much more rapidly on account of the greater dilution, so that after two hours' standing the liquid can be run into other tanks. Here the colour will take far longer (five to six hours) to settle down to such an extent that a fresh separation of the different degrees of fineness can be effected by baling. In twelve hours more a third (generally the last) baling is performed; and by this means the four tubs will then contain sediments of ultramarine of varying degrees of fineness, the first tub containing the coarsest particles, whilst in the fourth or last the colour is in such a finely divided state that it does not settle down completely when left to stand. This portion, therefore, has to be precipitated with saline solutions, for which purpose milk of lime, aluminium sulphate, alum, dilute mineral acids, &c., are used, these being added with continued stirring. When the resulting precipitate has settled down to the bottom the top liquid is syphoned off, and the blue paste is pressed. Generally the liquid first baled from the collecting tank will be added to the contents of the fourth washing tub for precipitation.

In ultramarine works the described levigating process is, of course, performed in a systematic manner. The washing tanks are placed in terraced rows, so that the liquids can be run off conveniently into the tanks below, until they finally arrive in the lowest of all, where the precipitation with saline solutions takes place. The coarse sediments remaining in the upper tanks are united, reground, and afterwards levigated again, either alone or with other portions of the same shade. In the same manner the sediment from the second row of tanks will be united for further treatment, viz., pressing, drying, and grinding. The same is done with the mass from the last two rows of tanks, so that in this way the whole batch of raw ultramarine blue stock is separated into three distinct grades of different fineness (and sometimes shade as well). According to the required fineness of the finished ultramarine blue, the sediments from the second and third rows of tanks may be wet-ground repeatedly, and levigated after each grinding, until finally the product attains such a degree of fineness that it will no longer settle down of itself and must therefore be precipitated by one of the abovementioned saline solutions.

The ultramarine paste obtained by the above method is *dried* in various ways in practice, inasmuch as in many places this operation is carried on in proper drying-rooms provided with all modern arrangements for ventilation and heating. Sometimes, however, the waste heat of the furnaces is used for this process, the large space above the tops of the furnaces being also utilised for drying. In the former case flat drying-hearths heated separately are used, the wet colour being placed in enamelled iron drying-pans. This arrangement requires special attention in order to avoid any risk of overheating, whereby a greenish shade is easily imparted to the blue. The drying-hearth is decidedly preferable on account of its far greater working capacity. In many manufactories, however, the above mentioned drying-pans are placed on suitable wide strong iron drying-frames in special drying-rooms heated by direct steam, whereby the drying process is, of course, a far more protracted operation than on the drying-hearths, though it generally furnishes a somewhat softer product.

For drying the blue paste on the surface of the furnace tops this surface must be covered perfectly smoke-tight with cast-iron plates about half an inch thick, so as to make a level floor. The heat is supplied by a flue, starting from the heating chamber of the furnace and ending below the centre of the drying surface, from which point the heating gases are conducted by smaller flues underneath the iron plates so as to heat all parts of the drying surface. All the flues communicate with a main, through which the hot gases finally escape to the chimney-stack. By this simple arrangement an equal temperature is obtained at all points of the drying surface, thus ensuring uniform drying.

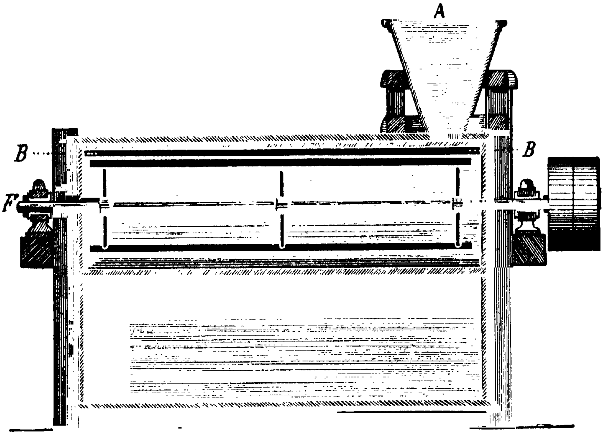
In many blue works a large part of the ultramarine blue is dried in air sheds, erected either in the open air or in suitable, easily accessible places upon the roof of the works, &c. Partly to protect the colour from the rain, and partly to keep up an equal and effective circulation of air, the side openings of the sheds are provided with adjustable louvres.

6. *Grinding, Sifting, and Mixing Ultramarine*

The dried ultramarine is in the state of more or less hard lumps, and must next be ground and sifted to obtain powder for sale, this being the only marketable form of the product. This operation, too, is carried out in various ways in practice. All types of colour-grinding machines are used for ultramarine with more or less success. To obtain a medium fine product from lump ultramarine blue that is not over hard the "chasseur" illustrated in Figs. 63 and 64 is the machine most frequently employed in ultramarine works.

On the other hand, very hard crude ultramarine is somewhat troublesome to work with this sifting machine, especially if a very fine product is required, the sieves then needing frequent changing, which sometimes causes a very considerable loss of time.

FIG. 63.

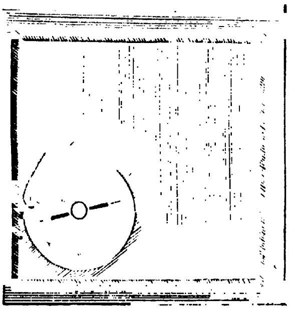


A, hopper. *B*, hoop iron. *F*, beater shaft (600–800 revolutions per minute).

The very fine brands of ultramarine (especially those obtained by the precipitating process) used by paper stainers, as well as for many other purposes, must be crushed and ground several times if necessary in small mills, and afterwards sifted in centrifugal sifting machines, or in bolting machines, to an impalpable powder. Nowadays very finely powdered brands of ultramarine are sifted in the Jasse sifter, illustrated in Fig. 51 and described on page 63, on account of its superior capacity. Ball mills with a continuous sifting device, especially the larger sizes, also give very good results in crushing hard brands of ultramarine, and present the additional advantage that no preliminary treatment is necessary. Of course, where a large output is in question a number of these machines must be installed in order to ensure regular and continuous working.

As it is not always possible to obtain products of uniform appearance and brightness from the furnaces, whereas customers naturally require constant qualities of ultramarine for their purposes, the products from a number of different batches must be blended in such proportions that the merchantable grades are always of uniform quality and shade. The relative proportions of the different raw materials needed to produce the required brands are first determined on a small scale, and these proportions are adhered to in mixing the bulk. The components being already in a pulverised state, it is sufficient to pass the thoroughly mixed product through a sifting machine again. In most cases the mixture is sufficiently complete to constitute a perfectly uniform product.

Fig. 61.



B, hoop iron. *F*, beater shaft. *S*, sieve.

In making cheaper brands of ultramarine blue the pure grades are mixed with a quantity of gypsum ranging between 10 and 50 per cent., according to the price of the resulting ultramarine. Gypsum being a distinctly crystalline body, of pure white shade, is difficult to mix so intimately with bodies of different shade that the mixture will appear uniform in colour. Moreover, in the case of ultramarine blue, which is of low covering power in comparison with some colours, the mixing must be performed with both substances in the dry state, and the operation is generally very troublesome and requires the greatest attention. Some kinds of ultramarine, too, are unsuitable for directly mixing with gypsum, so that care must be taken in selecting the shades to avoid mixtures which would afterwards be absolutely useless. The dark shades of ultramarine, especially those with a reddish tone (more rarely the green shades), suffer most from considerable additions of white substances (gypsum), the shade being lightened to such an extent in some cases that the product can no more be considered a merchantable article. Hence special precautions must be applied to mask this very unfortunate influence on the brightness of the resulting mixtures. This can be effected by admixing along with the gypsum a certain quantity of some hygroscopic substance, which will keep the colour constantly moist and thus counteract as much as possible the lightening influence of the white admixtures. Commercial glycerine, more rarely pale syrup, is generally used for this purpose in ultramarine manufactories. The simplest method is as follows: Assuming 400 parts of an ultramarine have to be mixed so as to contain 20 per cent. of gypsum, the mixture consisting, therefore, of 80 parts of gypsum and 320 parts of green-tinged ultramarine. In the first place the 80 parts of gypsum are mixed with about 20 parts of finest precipitated blue quite thoroughly, so as to colour it equally. The resulting mixture has then to be run, if necessary, several times through an edge-runner mill until a sample spread upon paper exhibits perfect uniformity of shade. This can now be mixed with the rest of the ultramarine much more easily, *i.e*, without any further grinding. It is spread out on a clean part of the floor to a uniform depth, and moistened with about 30 parts of a liquid consisting of 10 parts glycerine or syrup (or both together) and 20 parts of water, the moistened mass being then worked over thoroughly several times. The moistening is most effectually performed with an ordinary watering-can fitted with a rose. The uniformly moistened mass is sifted, preferably by hand, through a wide-meshed sieve, then spread out afresh and allowed to stand until the next day, whereupon it is run through a beating mill or through a sieve until no more dry particles can be detected. The prepared mass can now be mixed with the pure ultramarine blue, in any proportion. The weighed quantity of ultramarine, in the present case 320 parts, must be divided in two equal portions, and one portion thoroughly mixed with the damp mass by means of a shovel. The mixture is sifted again, but, being now less damp, can be put through a much finer sieve. The product, after having been allowed to stand twelve hours, is mixed in the same manner with the second portion of the pure ultramarine and sifted again, this time, however, through the finest sieve, the damp mass being able to pass without difficulty. The mixture obtained in this manner is indistinguishable from pure ultramarine in appearance, even when kept for a long time, whereby, although the greatest part of the admixed water will have evaporated, the shade will become even fuller. Provided these mixed brands, as in fact is always now the case, are sold by the manufacturers as lower grades at a lower price, there can be no question of adulteration, more especially as such brands are unobjectionable for many purposes (cheap paint, for instance). The case is, however, very different when—as seems to be now practised more frequently—the pure brands of ultramarine are mixed with gypsum or other cheap white mineral, coloured with blue aniline colouring matters. Products of this kind are inferior in value to genuine ultramarine, and are to all intents and purposes adulterations. Instead of adding glycerine and water, the appearance of ultramarine, and certain other colours too, can sometimes be improved by a small addition of vaseline, with which the colour must be mixed most intimately in grinding. Moist or greasy products appear darker than dry ones.

For testing ultramarine *Hoffmann** gives the following rules: Standard samples must be used for comparison. To examine the brightness and intensity of the colour, a small sample of ultramarine is spread out evenly on white paper with a polished metal or horn spatula, and a small sample of the standard type placed beside it and pressed down in the same way. If both colours be of equal shade they cannot be distinguished one from the other; but where any difference exists it will be readily distinguishable, the standard type being easily found the darker, lighter, more reddish or greenish, weaker or brighter, according to the character of the test sample. This test is a very accurate one. According to *Wunder*, the spectrum can be used for this purpose by placing a sample of the colour, ground in colourless varnish, on glass, and observing the absorption spectrum. The fineness of texture is determined by spreading a sample of the colour on paper with the finger. The finer the colour the longer the streak produced.

The colouring power can be tested by mixing each of the samples to be compared with the same quantity of china clay in a mortar. The stronger coloured mixture contains the ultramarine having the greater colouring power.

To test the power of resistance to alum, a small sample of the ultramarine is poured into a test glass with a concentrated solution of alum and shaken up repeatedly. The rate of decomposition shown by the fading of the colour can be watched and compared with the standard type treated in the same manner. The fineness of the pulverised pigments is of great importance in this test. Ultramarines that can resist alum are specially used by paper makers. Ultramarines coloured with blue coal-tar dyes can be detected by shaking up the sample with water and alcohol. The detection of other adjuncts entails a complete chemical analysis. A special characteristic of ultramarine is the fact that it is bleached by dilute acid, sulphuretted hydrogen being liberated.

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* Dr. R. Hoffmann, "Ultramarine," (Vieweg u. Sohn, Braunschweig.)

"Ultramarine sickness" is a phenomenon known to artists, whereby ultramarine ground in oil and used as a thick coating gradually becomes dead and bleached when applied thinly, more like a glaze or varnish. This phenomenon rarely occurs, neither is it observed when mixtures of ultramarine and white are used.

The chemical constitution of ultramarine is not exactly known, nor have its components been successfully isolated. Why this body, which is compounded from substances which, with the exception of the pale yellow sulphur, are colourless, should exhibit colour is also unknown, and little explanation is available of the part taken by sulphur in its formation.

In order to complete the subject, a few words on *violet* and *red ultramarine* may be given. Violet ultramarine is not a separate compound, but a mixture of blue and red ultramarine, constituting an intermediate stage in the manufacture of the latter from the former under the influence of sal ammoniac. The principle of its formation is based upon the action of dry hydrochloric acid and oxygen at 150° to 180° on blue ultramarine, the latter being deprived of sodium in the form of sodium chloride. According to *Grünzweig*, soda blue is mixed with about 5 per cent. of sal ammoniac, the mixture being then ground and placed in a furnace for twenty five hours at about 150°, the mass being stirred every half-hour. Ammonia and undecomposed sal ammoniac are given off. The blue is thereby converted first to a dirty violet shade, which afterwards becomes purer. After twenty-four hours the violet mixture is transferred to another part of the furnace, and heated four days longer at about 130°, whereupon the violet is ready for use in manufacturing ultramarine red, or to be put through a washing and grinding process for sale.

For making red ultramarine the violet product is put into a jacketed iron cylinder fitted with a stirring machine. Steam is admitted into the jacket and the contents of the cylinder heated to about 150°. Dry hydrochloric acid gas is next passed over the violet, which is kept in movement by the stirrers, and in the course of a few hours—if the right quantities have been used—the hydrochloric acid gas will be completely absorbed, and the red colour gradually developed. When finished, the red must be washed in alkaline water, dried, and ground. To obtain a purer and richer shade with a blue tinge, the red, which was initially somewhat yellowish, must be exposed to the air in a thin layer for several days.

On heating red ultramarine above 360°, or treating it with hydrochloric acid gas at a higher temperature than above mentioned, *yellow ultramarine* will be very quickly formed.

In the conversion of blue into violet by the process described sodium and sulphur are abstracted from the blue, whilst the latter takes up oxygen. On treating the violet further with hydrochloric acid gas in presence of air the content of sulphur will remain unchanged, but more sodium is abstracted and more oxygen taken up. During the conversion into yellow a further diminution of the sulphur content occurs.

The violet, red, and yellow ultramarines are of little practical importance, and their chemistry is still obscure.

(*d*) Blue Cobalt Colours

The members of this group are but very little used as colours in the true sense of the word, having been on the one hand entirely displaced by newer and more intensive colours, whilst, on the other, their high price has always been a serious obstacle to general application.

The blue cobalt compounds known in commerce as smalt, king's blue, cobalt blue, Leyden blue, Dumont blue, Thénard blue, cœlin, bleu céleste, &c., cannot be regarded as pigments in the true sense, since they are really coloured glass masses which only acquire the appearance of pigments on account of their very fine state of division. Consequently these colours lack the properties that pigments are usually required to possess, viz., a sufficient covering power, in addition to brightness of shade. This most important quality is entirely absent, and therefore the blue cobalt colours, apart from their very small use as artists' colours, are not used as oil or varnish paints. Nevertheless, from their chemical composition they are highly indifferent to all possible influences, especially high temperatures—qualities which enable them to be applied for colouring glaze fluxes in pottery, in the manufacture of stoneware, enamel, majolica, as well as in the glass industry; and, indeed, it is chiefly for these purposes that they are now produced. The cobalt colours, even such as are not blue, are made exclusively from cobalt ores, known in the trade (in an imperfectly roasted state) as *zaffre* or *safflower*. These are chiefly obtained from cobalt glance, consisting essentially of cobalt oxide, with variable quantities of arsenic, nickel, copper, and traces of manganese oxide, bismuth oxide, &c. According to the purity of the cobalt ores—*i.e.*, the content of cobalt oxide—safflower is graded into fine, medium, and ordinary. In commerce these three qualities are known by the following marks: FS or FFS, fine; MS, medium; and SO or OS, ordinary.

The cobalt ores are roasted in reverberatory furnaces, merely to convert the metals into oxides or sulphates, the formation of metal sulphides and metal arsenides also occurring to a small extent. When cobalt ores rich in arsenic are roasted, this latter element is oxidised and furnishes variable quantities of arsenious acid. To collect this product as a sublimate the furnaces are provided with flues, in which the product of sublimation is deposited in consequence of the lower temperature prevailing in the flues.

Smalt (*Smalte, Eschel*)

The oldest representative of the blue cobalt colours, smalt, was already known in the middle of the sixteenth century, at which time it was discovered by Schürer. When he sold his secret to England the first smalt mills were erected in this country, but all the cobalt ore was obtained from Saxony, so the mills soon had to be stopped when the Elector John I. prohibited the export of the mineral, and started the still existing first blue colour factory at Schneeberg, in Saxony.

The technical production of smalt is based on the capacity of cobaltous oxide to fuse with silica and potash to a deep blue coloured glass, which, when powdered and levigated, attains such a fine state of division as to be capable of use as a pigment. The manufacture of smalt is therefore divided into two quite separate stages, the fusing process and the crushing of the fused product.

Before entering on a description of the first operation, the fusing, the salient features of the composition of the glass charge must be referred to, even though briefly. Silica is mostly used for this purpose in the form of quartz, as free as possible from admixtures containing clay or lime, as these would cloud the glass and form impure colours. The alkaline flux for cobalt colours consists exclusively of potassium, mostly in the form of potash (potassium carbonate), though sometimes potassium sulphate is used. The corresponding sodium compounds, viz., soda or Glauber salt, although cheaper than potassium salts, cannot be used, since they form a bluish violet glass instead of the pure blue product obtained with potash.

It is of the greatest importance in compounding the glass mixture that the cobaltous oxide should form the sole colouring ingredient in the glass, for on this fact alone depends the purity of the resulting shades, which of course will be brighter in proportion to the amount of that oxide in the mixture. However, since the other metals contained in safflower—especially iron and copper—also give coloured glasses, the formation of the pure blue shades would be considerably disturbed by their presence, and care must therefore be taken to obviate the detrimental effect of these metals in the glass as far as possible. This can be effected by adding to the glass charge a quantity of arsenic in proportion to the weight of the cobalt ores, the arsenic being obtained, as described above, by sublimation in roasting the cobalt ore. In the course of the fusing process the arsenious acid encounters the metals iron, nickel, copper, &c., and forms the corresponding arsenides, which, being specifically heavier, separate from the liquid glass mass and settle down to the bottom of the melting-pots. The separated regulus, called cobalt regulus, contains nearly all the metals* which would have a detrimental influence on the colouring effect of the cobaltous oxide in the glass. The effectual separation of this regulus is therefore the crux of the whole fusing process.

The fusing of the glass charge is effected in glass furnaces of the usual type, viz., upright reverberatory flame furnaces, heated by direct fire, the melting-chamber being placed above the fire-grate. The melting-chamber is either square (rectangular) or oval in shape, and it is roofed over by a pointed or flat arch. The bed of the furnace is intersected lengthwise by a fairly broad channel, so as to leave on both sides a narrow strip or bench, on which are placed the glass pots filled with the charge for melting. Surround-

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* The regulus of cobalt consists of :

Nickel .	48·20 parts	Copper .	1·93 parts
Cobalt .	1·63 „	Arsenic .	42·08 „
Bismuth .	2·44 „	Sulphur .	3·07 „
Iron . .	0·65 „		

(According to R. Wagner.)

ing the glass pots, at the same level as their upper edge, is a brick wall, the ring, carrying the furnace top. Immediately below the latter, and in front of each melting-pot (of which each furnace usually holds eight to ten) is a working hole, through which the pots are charged and emptied and the contents stirred. The glass charge and ore being filled into the melting-pots, the mass is heated by a strong fire and frequently stirred until it has melted completely out. Without interrupting the firing, a short time is allowed to elapse for the regulus to settle down properly, and finally the liquid glass mass is baled out and poured into cold water. By this sudden cooling (quenching) the glass bursts into small friable lumps and granules ready for grinding.

The grinding and levigating are generally carried on at the same time. Formerly this was done in small stamping mills, but at present wet mills or medium-sized rolling mills specially arranged for this purpose, are used. The levigating process generally takes place on the same principle as already described for the ultramarine blue (*q.v.*). After levigation the fine smalt is dried and sifted in the usual manner. The commercial grades of smalt vary according to the fineness of the powder; and certain differences also exist with regard to their intensity. The darker and coarser-grained brand of smalt is called ordinary colour ("gros bleu"), the next finer and somewhat paler kind is sometimes called Eschel or "medium colour," and the palest and finest-grained levigation product is "fine colour." Smalt consists of:

66·2	to	72·11	parts	silica
6·75	„	1·95	„	cobaltous oxide
16·31	„	1·80	„	potash
8·64	„	20·04	„	alumina

Small quantities of lime, ferrous oxide and nickelous oxide, arsenious acid, &c., are also present. One part of cobaltous oxide will colour as many as 250 parts of glass a distinct blue.

Smalt is only slightly attacked by cold hydrochloric or nitric acid. Caustic alkalies have no action. Hot hydrochloric or sulphuric acid will extract a yellow-green solution.

Smalt is not entirely unaffected by water, semi-dissociated glasses of lighter and dirtier shade being therefore formed in the levigating process. Water also causes the smalt to become sandy, on which account the washing and levigating process must be performed with care.

Smalt is adulterated with gypsum, clay, and ultramarine (revealed by the acid test).

Cobalt Blue

(*Cobalt Ultramarine, Cobalt Blue, Thénard or Leyden Blue, King's Blue*)

With regard to its chemical composition, this colour is a compound of cobaltous oxide and alumina, or of both, with variable quantities of zinc oxide. Whether the latter enters into combination entirely or whether only a portion of it is chemically combined need not be discussed in this place. At all events, the grades of cobalt blue containing zinc oxides show a striking difference in external appearance. The cobalt blue prepared from alumina and cobaltous oxide only is always of a reddish shade, whilst the kinds obtained with zinc oxide are of a pure greenish-blue shade, according to the amount of zinc oxide present. As in the case of smalt, the pigmentary material is cobaltous oxide. The colour is best obtained by subjecting a mixture of alum and cobaltous sulphate alone or combined with zinc sulphate to strong and protracted calcination. Cobalt blue can also be produced by heating dry alumina with other salts of cobaltous oxide, such as cobaltous nitrate or phosphate, but the product is more expensive than that obtained by the first method. The compound has now no technical value, and is only used for obtaining special effects by artists and in porcelain painting. It was formerly used as a water and oil colour, in colouring artificial flowers, and for printing bank-notes, &c. (being very difficult to reproduce photographically). The commercial brand is U, the various grades being FFU, MU, OU.

Another blue cobalt colour, cobaltous stannate, known as *Cœruleum, bleu céleste*, &c., is exclusively used as an applied artist's colour. It is obtained by heating cobaltous sulphate, tin salt, and chalk, and consists then of cobaltous oxide with variable quantities of tin oxide and calcium sulphate. This is the only cobalt colour that covers well without being granular. It is suitable for oil painting, and is specially used for painting skies. Unlike the other cobalt pigments, cœruleum does not seem to have a violet tinge by lamp-light.

In accordance with the very divergent chemical composition of the blue mineral colours, their technical application is of a highly varied character. Considering in the first place the two chief uses of the colours in general—as oil paints and distempers—the blue copper pigments are entirely unsuitable for mixing with varnish, though to a certain degree considered to be very durable when used with and upon lime. The exact contrary is the case with regard to the ferrocyanogen pigments. These form an extremely good material for painting in oil, especially in their mixtures with white and yellow pigments, whereas their resistance to lime is practically *nil*. Between these groups of colours come ultramarine blue and, to a certain degree, the blue cobalt colours as well. Whilst the first, however, are used as oil or lime colours indifferently, the high cost of producing the cobalt colours, as already mentioned, militates against their general application, and hence they are restricted to artist's colours. Some importance, however, attaches to their application for painting on stone-ware and porcelain, where they produce effects that cannot be imitated by any other products.

Blue copper colours cannot be used for painting with oil and varnish because of their low covering power, and, more especially, their strong tendency to saponify with fatty acids. The rate of this saponification varies according to the more or less stable combination of the blue copper salts, but always results in a greening of the pure blue and consequently very delicate shade of these salts. The very low stability of the copper compounds with hydroxyl and carbonic acid (such as are here in question) specially facilitates the formation of copper soaps with the fatty acids of linseed oil, and consequently these paints are most liable to decompose rapidly in the manner specified.

On the other hand, the formative process of the ferrocyanogen colours by means of the strongest mineral acids or compounds acting in the same manner renders the products absolutely insensitive to all acid influences, and still more so, of course, to those of the weak fatty acids. This property renders the ferrocyanogen colours excellent materials for mixing and shading nearly all pigments, their high covering power being also a specially important factor. Ultramarine blue does not possess these advantages in the same measure, its covering power being very inferior as compared with Prussian blue, whilst the high sulphur content of ultramarine almost entirely precludes a mixture with most other pigments, especially those containing lead, which are very important technically. Although in such cases the formation of black lead sulphide does not take place at once, it will ensue in course of time in paints made from such mixtures, and the more so the larger the quantity of ultramarine present in the mixed colour. For this reason it is inadvisable to add even small quantities of ultramarine blue to white lead in grinding in order to remove its peculiar yellowish shade, for when dry such paints tarnish to a greater extent in a relatively short time than those made from pure white lead. Moreover, apart from the injurious effect of its sulphide sulphur, ultramarine is unsuitable for producing green mixtures, on account of its tone, even the palest shades of ultramarine blue being nearly violet when compared with the greenish blue shade of the ferrocyanogen colours. Hence when mixed with pale yellow (for instance, cadmium yellow, which is indifferent toward ultramarine) it always gives olive-green shades only. Though this property of ultramarine unfits it in general for oil paints, where almost exclusively mineral colours are used, it is of all the greater value for obtaining a variety of olive-green shades in the manufacturing of wall and fancy papers, where the yellow mineral colours are replaced by leadless yellow lakes. Here also the far greater covering power of ultramarine blue in distemper paints comes into prominence. With regard to the use of blue mineral colours for lime washes, ultramarine naturally takes the first place, since the less covering and more delicate shaded blue copper pigments can only be used to produce especial effects unobtainable with the reddish ultramarine shades.

Fastness to light is a property shared equally by all blue mineral colours.

The use of Prussian blue in green mixtures will be discussed later on in connection with the chrome and zinc greens.

GREEN MINERAL COLOURS

According to the raw materials used in making the green mineral colours, these can be divided into three classes: *copper*, *chrome*, and *ultramarine green colours*. With regard to the first of these, copper sulphate is now the sole raw material used in their production. To prepare the numerous and highly varied chrome green colours, however, potassium chromate is used as well as the cheaper sodium chromate. The application of ultramarine green—which, as we have already seen, is really an intermediate product in the manufacture of ultramarine blue—is now almost discontinued, and is therefore relatively unimportant.

Of the green copper pigments only three representatives are at present of importance; verdigris, Schweinfurt green, and certain by-products, the so-called lime-arsenic greens, which, however, are going more and more out of use, for various reasons. The shades of these pigments can be exactly imitated by certain new lakes, whilst, on the other hand, the highly poisonous nature of the pure copper colours, and still more so of the copper arsenic colours, greatly restricts their general application, apart from the consideration of their relatively high cost of production.

The chrome greens also may be divided into different varieties, chrome green proper (oil green, green vermilion), zinc green, chrome oxide green, permanent green, &c., being the most important and best-known kinds. Only the chrome oxide greens are natural colours, the others being mixtures from yellow and blue, chrome greens from chromes and Prussian blue, zinc greens from zinc chrome and Prussian blue, permanent greens from zinc or chrome yellow and chrome oxide green.

On comparing the most prominent qualities of the different varieties of green mineral pigments, it is found that chrome oxide green and the permanent greens prepared therefrom are very fast to light and atmospheric influences. Nearest to these come all the green copper pigments and the ultramarine green, which latter, containing sulphur, is specially insensitive to the detrimental influence of sulphuretted hydrogen gas, so destructive to many metallic colours. Then follow the zinc greens, and finally the chrome greens, which have a very low power of withstanding the influences in question. This also applies to the stability of green mineral colours in lime washes. With regard to their covering power in oil paints, as well as suitability for water colours, the chrome greens take first place, followed by the zinc, chrome oxide, and permanent greens, whilst ultramarine green and the copper green colours come last of all.

(*a*) GREEN COPPER COLOURS

Verdigris (*Vert de Gris, Grünspan*)

Verdigris (copper acetate) cannot be considered a colour in the true sense, being a crystallised salt largely soluble in water. Nevertheless its different varieties, when pulverised and ground with varnish, are extensively applied in many countries for painting on metals, *e.g.*, sheet iron, which it protects very effectually against rusting. Of course, it is not applied in a pure state, since, being crystalline and more or less transparent, it gives only glaze paintings, and must therefore be mixed with covering pigments having no effect on its shade, such as white lead, zinc white, lead sulphate, &c. Similar paints can also be used on wood, for which they act as an excellent preservative.

The manufacture of verdigris was originally carried on exclusively in France. Thence, in time, when it came into great demand on account of a lack of other green mineral colours, it spread gradually to other countries, especially those where viticulture was extensively practised. The product, however, was always inferior to the French article, which is even now regarded as the best. From this circumstance the method of producing verdigris was long enveloped in mystery and considered to be very difficult. This is, however, by no means the case, the manufacture of this salt being, on the contrary, a very simple process, and in many parts of France is conducted on very primitive lines.

The French method of manufacturing verdigris—in former times a kind of domestic industry—is very similar to the Dutch white lead process. Before entering, however, on a description of the method it is necessary to devote attention to the most important properties of verdigris and its chemical composition.

Verdigris is copper acetate, of which there are technically two kinds, *basic* and *neutral* verdigris. The former is blue in colour, and is generally considered to be a compound having the formula $Cu(C_2H_3O_2)_2.Cu(OH)_2 5H_2O$. There is, however, a second commercial basic verdigris too, distinguished from the former by a more decided greenish tinge, and probably having the formula $Cu(C_2H_3O_2)_2 2Cu(OH)_2$.

Neutral verdigris (so-called distilled, but more properly termed *crystallised* verdigris) is obtained by dissolving the basic compound in acetic acid, or by decomposing copper sulphate with sugar of lead (lead acetate) or calcium acetate, whereupon lead sulphate or calcium sulphate (gypsum) is precipitated as an insoluble by-product :

$$\underbrace{CuSO_4}_{\text{Copper sulphate}} + \underbrace{Pb(C_2H_3O_2)_2}_{\text{Sugar of lead}} = \underbrace{Cu(C_2H_3O_2)_2}_{\text{Neutral verdigris}} + \underbrace{PbSO_4}_{\text{Lead sulphate}}$$

or

$$CuSO_4 + \underbrace{Ca(C_2H_3O_2)_2}_{\text{Calcium acetate}} = Cu(C_2H_3O_2)_2 + \underbrace{CaSO_4}_{\text{Gypsum.}}$$

The neutral verdigris exists in commerce in the form of "grapes" of magnificent dark green opaque columns, whilst the basic salt is put on the market in the form of balls, loaves, &c., as well as in cylindrical packets, covered with leather or strong grey packing paper. In this state the basic verdigris is very tough and solid, being otherwise very difficult to crush. Very good and well-matured sorts exhibit an earthy or foliaceous fracture, and radial fracture traversed by small brilliant crystal plates is also a highly appreciated indication.

In *the French process* of making verdigris metallic copper is gradually converted into basic copper acetate by vinegar obtained from the fermentation of grape husks. The method is capable of numerous modifications, and in France the process varies according to the district and the extent of the wine-growing industry. In all cases it is primarily essential to store the grape husks in such a manner as to ensure complete fermentation, and afford the possibility of working satisfactorily the whole year through with the accumulated store of material. The selection of the husks for this purpose is by no means a matter of indifference. The most suitable ones are those coming direct from the wine press, whereas those husks that have been steeped in water repeatedly, or even once, and pressed out again are mostly useless, being unable to ferment from lack of sugar, and, in fact, liable to rot in a very short time.

The fresh husks are stored either in large open casks or in specially airy, dry rooms floored with glazed earthenware plates. The husks are spread thereon, well stamped down, and left. The acetic fermentation usually ensues in the course of a few weeks, sometimes sooner with husks of good quality. In any event, however, the husks are useless for the purpose in view unless a distinct aroma of vinegar is given off at the commencement of fermentation.

In the simplest process the husks are portioned out in earthenware vessels as soon as this condition has been attained, and circular or coiled thin copper sheets are inserted into these vessels in such a manner as to be surrounded on all sides by the husks. Before immersion the copper sheets must sometimes be put into a solution of verdigris in vinegar, then dried, heated, and covered with the husks, this treatment assisting to start the formative process. The vessels are placed in a uniformly warm room, in cellars, holes specially dug for this purpose, &c. When a sufficiently thick coating of verdigris is formed on the surface of the copper sheets, which sometimes takes a considerable time, it must be scraped off, the verdigris being then collected, kneaded with water into a homogeneous mass, pressed in bags of leather, strong paper, or pasteboard, dried, and put on the market. The copper sheets, after being cleaned from the verdigris, can, of course, be used again until completely decomposed.

The arrangement is different when the manufacture of verdigris is carried on directly in closed rooms, the use of earthen vessels being avoided. In this case the copper sheets, which are generally thicker than in the other case, and flat, must be placed in rows side by side upon a layer of husks, and are covered with another layer of husks. This alternation of copper plates and husks is repeated until the mass has reached a height of 32 to 40 ins. It is not advisable to go higher, since the pressure on the lower parts would then be too great, and the successful course of the process might be endangered. Care must also be taken that the copper sheets do not come into contact, but are covered evenly by the husks. The reaction of the vinegar on the metallic copper generally begins at once, and in the course of a few days the sheets will be covered with a distinct coating of verdigris, the formation of which then progresses in the same proportion as the temperature of the room is more or less favourable. For this reason the progress of the reaction must be carefully controlled, and care must be taken to suitably modify the temperature whenever an interruption or retardation of the process occurs. If in the course of three to five weeks the husks are found to be completely exhausted of acetic acid, there is nothing to be gained by leaving the metal any longer, and therefore the copper sheets covered with verdigris may be scraped as already described, or else are moistened with warm water and put on frames for about three weeks in a moderately heated room, where they are kept constantly damp by a small current of steam. Under this treatment the hard crust of verdigris on the copper becomes soft by absorption of water, swells up, and can be separated from the metal very easily by scraping it with copper spatulas. The further treatment of the verdigris is the same as already described.

The same result can be obtained much quicker by replacing the copper sheets by coarse copper filings, as is done in certain French manufactories. The filings must be thoroughly mixed with the husks already producing vinegar, and placed in large glazed earthenware vessels in cool rooms. After a few days the mixture grows warm, the heat increases more and more, and in the course of about a week the reaction will be in full swing. It is complete as soon as the heat diminishes and only a faint smell from vinegar can be detected, the husks then feeling nearly dry. The mixture is afterwards dried on shallow trays in the open air. Finally the verdigris is freed from husks in a suitable jigger, and ground in pug mills to separate the still undissolved particles of copper, packed in barrels, and sold in powder form. Mention has already been made of a modification of basic verdigris, distinguished from the verdigris obtained by the above-described process not only by an essentially more greenish shade, but also in point of chemical composition. This verdigris, which probably has the formula $Cu(C_2H_3O_2)_2.2Cu(OH)_2$, is obtained by the direct action of acetic acid on metallic copper. The copper is used in sheets about $\frac{1}{8}$ in. thick, coated with a solution of verdigris in vinegar, and then laid one upon the other in regular layers alternating with flannel rags of the same size dipped in acetic acid. At intervals of three days the layers are taken apart, the flannel rags soaked afresh with vinegar and replaced with the copper sheets as before. This must be repeated until the surface of the metallic sheets exhibits small crystals, which will generally be in two to three weeks' time, according to the temperature of the workroom. Procedure is now modified, the taking down and rearranging of the layers being repeated only every six days, whilst a more dilute vinegar is used for moistening, and a couple of small rods are placed between the flannel pieces and the metal sheets, so as to keep the copper with the damp flannel rags out of mutual contact. The copper sheets covered with verdigris must now be dipped, previous to repiling, in lukewarm water for a short time. At a moderate temperature (15° C.) this rather troublesome process will be finished in seven to eight weeks, the formation of verdigris having proceeded so far as to render its removal from the metal (by scraping) profitable.

Neutral verdigris, $Cu(C_2H_3O_2)_2$, known in the trade as "distilled or (crystallised) verdigris," is also manufactured by various methods, all, however, culminating in the concentration and crystallisation of the resulting solution of copper acetate. In some works this solution is prepared by treating basic verdigris with about its own weight of 32 per cent. acetic acid (specific gravity 1·045). As the resulting solutions may contain various impurities, such as grape husks, seeds, &c., they must always be filtered before concentration. This latter operation is preferably carried on in copper retorts provided with a receiver for recovering the volatilised vinegar. When the concentrated solution of verdigris marks a density of 20° Be. it is then ready for crystallising. It is poured into crystallisation vats, generally shallow, rectangular oaken chests. Small round wooden sticks, with cross-pieces fastened on the lower end, are suspended in the liquor, and on these the verdigris is deposited as crystals. The larger the sticks, the larger the "grapes" arise, and the more accelerated the crystallisation process.

Of those processes for making neutral verdigris by decomposing copper sulphate with calcium acetate, barium acetate, or lead acetate, only the first one will now be described. The other two are rarely employed, and, besides, they exhibit no difference of procedure or result, excepting perhaps in the higher cost of the product.

By treating copper sulphate with the equivalent quantity of calcium acetate, calcium sulphate is precipitated in the form of a white crystalline mass, settling down to the bottom of the tank on standing, and thereby allowing the solution (of copper acetate) to be separated by decantation. Calcium sulphate (gypsum) being soluble in cold water more easily than in hot, especially when in such a finely divided state as it is here, the reaction is preferably conducted at boiling temperature. The continued heating of the liquids being, however, impracticable on account of the expense, the precipitation of gypsum is incomplete, as will become evident when the solution of verdigris is being concentrated, the previously clear solution then depositing considerable quantities of gypsum, partly as a loose precipitate on the bottom of the evaporating pan, and partly as a hard incrustation on the sides, thus necessitating sometimes an increased consumption of fuel. For these reasons preference is given to methods (described later on) for obtaining verdigris by means of copper carbonate, as an intermediate product, or directly from metallic copper and acetic acid, no artificial heating being necessary.

Copper sulphate is easily obtainable pure in commerce, viz., especially free from compounds of iron. The calcium acetate, however, must generally be made in the colour works. The cheapest way is by dissolving pure quicklime, in the form of a thin milk of lime, with the corresponding quantity of acetic acid. For this purpose pure commercial pyroligneous acid is diluted with water to form an 8 to 10 per cent. solution, and the already prepared milk of lime is run into this dilute acid, with continued stirring, until the latter is completely neutralised, viz., until a small piece of blue litmus paper dipped into the liquid is no longer turned red. The solution of calcium acetate is then allowed to stand in the working tank (preferably a suitable large wooden vat) until sufficiently clarified.

Meanwhile, preferably in the same tank that is used for the conversion into verdigris, a solution of copper sulphate is prepared by dissolving the weighed quantity with ten times its own weight of hot water and heating (by introducing steam) and continually stirring it until complete solution is effected. The clarified solution of calcium acetate, having been heated in the same manner in another tank, is next poured slowly into the boiling solution of copper sulphate, the stirring and admission of steam being continued, care being taken to keep the temperature of the liquid at boiling-point. The precipitation of the gypsum begins at once, and continues on the further addition of calcium acetate, until the whole of the sulphuric acid is combined by the calcium. To ascertain this point exactly small filtered samples of the boiling liquid must be tested when the end point of the reaction is presumably neared. If on adding calcium acetate a white precipitate of gypsum is still formed,* more calcium acetate is needed. If, however, the calcium acetate be already in excess, a fresh addition of copper sulphate must be given. Of course it will be preferable to determine beforehand the exact content of solid calcium acetate in the solution, which can easily be done by means of the table given at the end of the book, and calculate therefrom the necessary quantity of sulphate of copper to be added for the precipitation.

The reaction being finished, the hot liquid is allowed to stand for a few hours, steam being shut off. The precipitate will usually settle down completely, and the clear solution of copper acetate can be drawn off into the evaporating retort. The precipitate of calcium sulphate in the tank retains a little of the solution of verdigris, and has to be washed out, therefore, at least three times with hot water. The first of these washings, if not too dilute, may be added to the evaporating liquid, the second is used for dissolving a fresh quantity of copper sulphate, and the third, which is, of course, the weakest in copper, can be used for washing out the precipitate of gypsum obtained from the next batch.

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* The copper cyanide test, as described in the manufacture of Bremen blue, may be used here.

In *Russia*, where a considerable quantity of crystallised verdigris is still produced, preference is given to the two following processes, which undoubtedly furnish a perfectly pure neutral verdigris. In the one process a solution of copper sulphate is precipitated with soda or potash, forming basic copper carbonate, which is dissolved in acetic acid whilst still moist from the press. In the second method this solution is produced by the direct treatment of copper filings with acetic acid.

$$\underbrace{2CuSO_4}_{\text{Copper sulphate}} + \underbrace{2Na_2CO_3}_{\text{Soda}} + \underbrace{H_2O}_{\text{Water}} = \underbrace{Cu(OH)_2.CuCO_3}_{\text{Basic copper carbonate}}$$

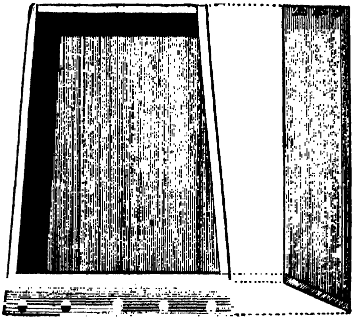
$$+ \underbrace{2Na_2SO_4}_{\text{Glauber salt}} + \underbrace{CO_2}_{\text{Carbonic acid}}.$$

The first process requires a vat 80 ins. in diameter and the same in height, together with a second one of about half the above dimensions. These vats are placed side by side, so that the liquids can be easily poured from the smaller into the larger one. The latter, the precipitating vat, is about a quarter full of hot water, in which a bag (about 3 cwt.) of Swedish copper sulphate is dissolved by continued stirring. In the meanwhile the small vat has been charged with 3 cwt. of soda, dissolved in hot water by stirring, the vat being then filled with cold water to the top. After a thorough stirring the solution is allowed to stand, the solution of copper sulphate being diluted with enough cold water to fill the vat half full. As soon as the solution of soda is sufficiently clear it is run slowly and in a thin stream into the solution of copper sulphate, with continued stirring, which is maintained for an hour after precipitation. The completion of this process can be tested with copper cyanide as described in the case of Bremen blue. Any excess of soda must be avoided, as it would turn the precipitate black and retard its solution in acetic acid.

The greenish-blue precipitate of basic copper carbonate having subsided, the top liquor, a solution of sodium sulphate, is run away into special evaporating pans for the recovery of the Glauber salt. The copper carbonate is washed out with pure cold water until a solution of barium chloride gives merely a faint cloudy precipitate of barium sulphate. The precipitate is then pressed (in a filter press) to a paste containing 30 to 40 per cent. of water, the press-cakes being transferred to a large square oak vat and treated with about 200 lbs. of dilute acetic acid (5° B.), added by degrees, the mass being thoroughly well mixed after each addition, and care taken to prevent loss by frothing over. When the whole is dissolved a solution of neutral verdigris is obtained of 7·5 to 8° B. strength, which must be concentrated to 20° B. and treated as already described.

The second method, in which metallic copper is dissolved in acetic acid, can be performed in various ways, the following being preferred: The dissolving of the metallic copper in acetic acid is effected gradually in dissolving vats, about sixty pieces of which, in the case of large works, are placed in one room and kept at a constant temperature of 25° to 30° C. These dissolving vessels are wooden chests (see Fig. 65) 30 ins. wide in front, narrowing to 24 ins. at the back. The length is 40 ins., the depth 4 to 6 ins., and the walls $1\frac{1}{2}$ to $1\frac{3}{4}$ ins. thick, of white beech or ash board. These are mounted in sets of three on a table sloping with a forward slope of about 2 ins., the wide ends of the vats, provided with five to six circular openings for drawing off the solution, being in front. The solution is drained into long, narrow, and strongly made oak vats placed underneath. The dissolving vats are charged with copper filings, and a certain quantity of acetic acid of 4° B. strength (equally divided between each three vats) is slowly poured in with wooden or copper ladles so as to moisten the copper filings uniformly. The copper is partly dissolved, and the solution runs through the openings of the chests into the vessel underneath. When the weighed quantity of acetic acid is exhausted the copper filings are treated with the solution from the collecting vat, and this is repeated until the solution measures 8° B. The end of the reaction is ascertained by the frothing of the solution. Sometimes the copper filings become very hot, in which case, to avoid loss of acetic acid, the pouring process must be accelerated. The whole operation lasts about five to six days. If the solution of verdigris has then attained a density of 8° B. it will be ready for concentration.

FIG. 65.



The concentration must be carried on in such a manner that the liquor does not froth up, since this indicates risk of decomposing the verdigris; and the process must be suspended when the concentration reaches 20° B., any excess beyond this limit being likely to cause premature separation of the salt. The process is always attended with a volatilisation of vinegar, which, as already mentioned, is recovered in the receivers of the concentrating pans, and this loss of acetic acid should be replaced by adding a certain quantity of vinegar before proceeding to the crystallising stage.

Verdigris can only be used as an oil colour, and is even then unreliable, being subject to discoloration by the chemical reaction of the fatty acids with the copper. This is particularly noticeable with the blue modification. Pure verdigris dissolves entirely in acids without any effervescence, and the ammoniacal solution exhibits a magnificent deep blue shade. Toward gas containing sulphuretted hydrogen verdigris is quite as sensitive as the lead colours; and it has an even more poisonous effect on the animal organism.

Emerald Green (*Mitisgreen, Schweinfurtgrün, Vert de Paris*)

Of all known mineral colours scarcely one—ultramarine blue perhaps excepted—can be compared in beauty and brightness with the brilliant shade of emerald green. Whilst nearly all shades of the known mineral colours can be imitated by means of coal-tar colours, none of the green lakes obtained from organic colouring matters is bright enough to bear comparison with emerald green. Unfortunately, however, emerald green, on account of its high content of arsenic, is one of the most poisonous colours known, if not *the* most poisonous of all. On this account its application is a very limited one and for many purposes prohibited in some countries by law.

In a pure state emerald green cannot be produced in so many different shades as, for instance, ferric oxide, or even the chromes. The difference between the various commercial brands is only in the finer or coarser state of the crystals, determined to a certain degree by the method of manufacture.

Emerald green, a compound of neutral copper acetate with copper arseniate, with the formula $Cu(C_2H_3O_2)_2.3Cu(AsO_2)_2$, was first manufactured at W. Sattler's colour works at Schweinfurth, in 1814, from basic verdigris and arsenic. According to other reports, von Mitis, of Vienna, was the first manufacturer. Liebig too published a manufacturing process in 1822. The strikingly bright shade and the consequent great popularity of the colour led to emerald green being made by nearly all colour-makers of importance, and this circumstance accounts for the various names given to emerald green, according to the place of production, very few of which names, however, are now in use.

The names *Emperor green, new green, mineral green, original green, patent green, Paris green,* &c., now very rarely employed, were invented by makers or merchants partly with the intention of leading a suspicious public to believe that non-poisonous products were in question. On the other hand, these names often apply to distinct mixtures of true emerald green with barytes, gypsum, chromes, or lead sulphate, added to lower the somewhat high cost of production, and also for toning the colour to a certain extent.

The manufacture of a perfectly handsome emerald green is one of the most difficult problems in colour-making. The chief difficulty is to allow the green a sufficient time for undisturbed crystallisation, since on this the brightness of the shade primarily depends. At the first glance this seems to be much easier than is really the case, for, apart from the necessary quietude, a thorough working of the mass is absolutely necessary to obtain a uniform product. It is very difficult even in the direct crystallisation of salts from their solutions to obtain perfectly equal crystals—it can never be done on a manufacturing scale; and this difficulty is still further increased with such a complex compound as emerald green, which is not crystallised directly from solutions of the raw materials, but from a flocculent and often slimy, dirty coloured precipitate of the raw materials. This is still further aggravated by the fact that the utility of the product as a colour, and therefore its commercial value, depends on the uniformity of the crystals, since, like all coloured crystalline salts, emerald green is paler in shade in proportion as the crystals are finer. Moreover, owing to carelessness, it may happen that no crystals at all are formed, an insignificant whitish green substance being obtained instead of the expected magnificent green. The causes of this accident are various. The use of insufficient quantities of water in the manufacturing process may have an unfavourable influence on the formation of the crystals; the precipitation temperature may be too high, or the mixture may be stirred too much or at the wrong time. The water, too, used for this purpose plays a very important part in the obtaining of successful results, as does also the nature of the raw materials. The water should contain a minimum of lime, and no iron at all; whilst the raw materials must be free from impurities, for which reason they must therefore be tested beforehand.

The injurious properties of emerald green necessitate specially strict precautions for the safety of the workmen engaged in the production, sorting, packing, &c. For the same reason the work should only be entrusted to those whose intelligence affords a certain guarantee that the prescribed measures for safety will be thoroughly carried out, and that dangers arising from ignorance, idleness, or carelessness will be prevented. According to experience, most cases of poisoning arise with workmen who have no sufficient knowledge of the dangerous character of the products with which they are working.

Hence the manufacture of emerald green must be confined to rooms which are separated from the other workrooms, and are lofty and airy enough to afford a sufficient protection to the men. The only materials now used are copper sulphate, arsenic (arsenious acid), soda, and vinegar, the older recipes, limited especially to the use of basic verdigris and arsenic, having been discarded. With regard to the plant, all the methods are based on the same principle: the raw materials are dissolved separately, in special tanks, and the solutions united in a third shallow vat underneath, which also serves for the crystallisation process, washing, mixing, &c.

The dimensions of the vats naturally depend on the extent of the works, but a certain limit is imposed by the uncertainty of the crystallising process when the vats are too large. For a medium production of 3 to 4 cwt. daily the following dimensions are suitable: The precipitating tank, which is shallow in order to facilitate crystallisation by increasing the superficial area, has a diameter of 7 to 10 ft. and a depth of barely 30 ins., and should be arranged so that the dissolved raw materials can be quickly and conveniently introduced. For dissolving the arsenic and soda a vat about 5 ft. in diameter and 40 ins. deep is required; for the verdigris (copper sulphate), which must be dissolved separately in a minimum of water, a vat 30 ins. wide and the same in height must be provided. If sufficient room is at disposal a special vat should be provided for the vinegar, about the same size as that for the arsenic and soda. If, however, this cannot be done the arsenic tank must also be used for the vinegar.

Besides the mentioned vats, all provided with steam pipes, two more are necessary for the blue top liquor, which still contains a good deal of copper. These vats must be placed so that the top liquor can be run in easily direct from the precipitating tank.

All the dissolving tanks, including that for the vinegar, must therefore be placed so that the outlets are above the edge of the precipitating tank, whilst the two last mentioned vats must be let into the earth, if, as is generally the case, the working room is on the ground floor.

In order to prevent increased danger to the workmen by unnecessarily

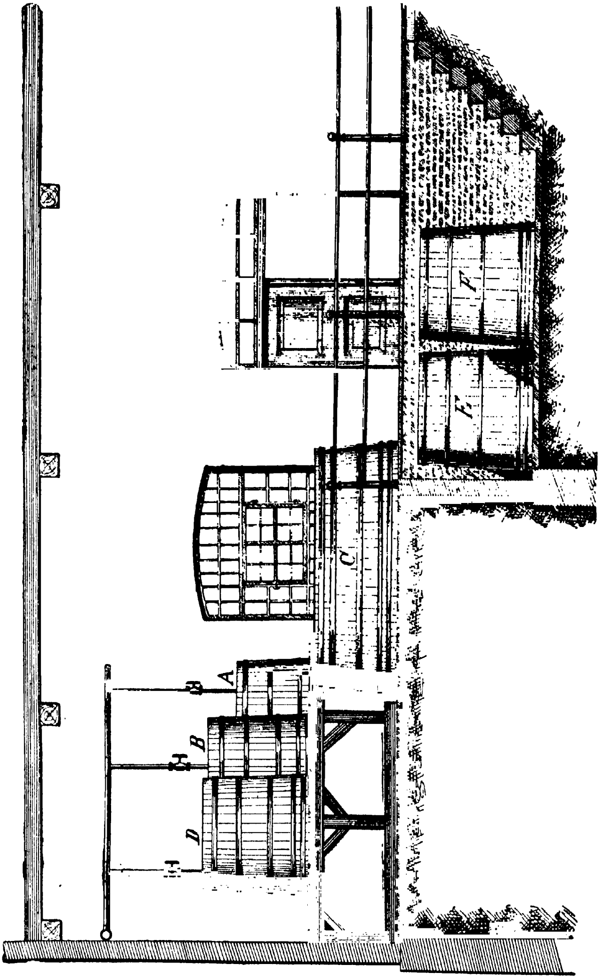


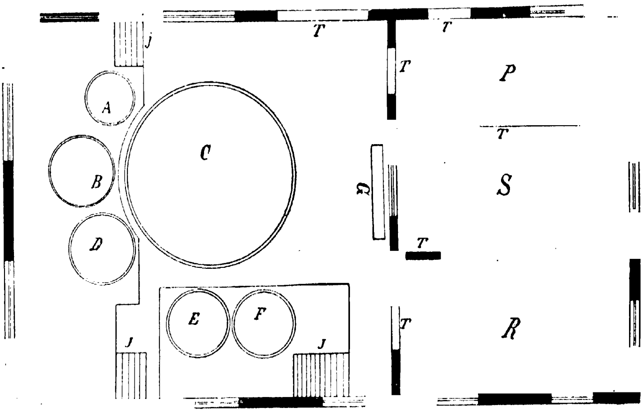
FIG. 66.

carrying about the pressed or dried colour in rooms situated outside the factory, it is advisable that the drying, sifting, sorting, and packing rooms should communicate directly with the chief working room, as shown in Fig. 67 (ground plan).

Although the old (Schweinfurt) method is now obsolete, it may be described here for the sake of completeness, the more so because it seems to afford the best means of explaining the more complex method of production from copper sulphate, arsenic, soda, and vinegar, to be described later on.

The arrangement of the dissolving tanks and the precipitating and crystallising vats is the same as mentioned, except that smaller sizes are used. Formerly the verdigris and arsenic were dissolved in separate large copper pans set in brickwork, over a fireplace, side by side, and the finished solutions were transferred to a vessel for further treatment. This arrangement, however, has no influence on the result. Certain difficulties are caused by dissolving the arsenic with the aid of steam, but these are easily remedied. The method of working is as follows:

Fig. 67.



T, *T*, doors.
G, press.
E. *F*, vats.
J, *J*, stairs.
P, packing room.
S, sifting and sorting room.
R, drying-room.

The smallest dissolving vat (*A*) is charged in the evening with 154 lbs. of crude French verdigris, crushed very small, and about 55 galls. of hot water, and left to soak all night. Next morning the arsenic vat (*B*) is filled with 110 galls. of water and heated to boiling by introducing steam. By-and-by 220 lbs. of white, finely ground arsenic are stirred in, solution taking place very slowly and necessitating continued boiling. The admission of steam must be checked as soon as the boiling-point has been reached, in order to prevent the liquor boiling over. The volume of the arsenical liquor is increased by the condensed steam, the dissolving process being thereby greatly facilitated. In four hours' time the operation will be finished. To make sure that the arsenic is completely dissolved, a sample of the liquid in a test glass must be examined for a sediment of undissolved arsenic on standing, and, if such be the case, the boiling must be continued until the solution is perfectly complete. This being attained, the liquor is made up with cold (or, better still, hot) water to a mark on the vat (generally a broad-headed copper or brass nail) corresponding to a volume of about 320 galls., heat being then applied until the liquid boils.

Towards the end of the arsenic dissolving process the heating of the soaked verdigris must be commenced, but the temperature must not be raised above 80° C., or, as already mentioned, the volume of water supplied for soaking the verdigris, being insufficient to give a solution of the most suitable condition for precipitation, must be made up gradually to 110 galls. in the same way as described for the arsenic. The liquid must be thoroughly well stirred, since the verdigris never dissolves completely, but only forms a pasty mass with this quantity of water. This paste should, however, be quite uniform, perfectly free from lumps or fragments of solid verdigris, since these, if ever so small, would not be decomposed by the arsenic, and in the most favourable circumstances would contaminate the resulting green.

The arsenic solution (after standing for some time) is united with the now liquid verdigris in the shallow precipitating tank *C*. This can be performed in two different ways. In the one about two-thirds of the dissolved arsenic is run into the precipitating tank, and is immediately followed by the verdigris liquor. This unavoidably cools the arsenic solution, a slower crystallisation and a darker green being the result. In the other the taps of both dissolving tanks are opened at the same time, so as to unite the solutions immediately, each of them being run through a brass sieve to retain any impurities. Even in this latter and most frequently employed method it is a general rule to run in only two-thirds of the arsenic solution at first, the remainder being added in the course of two to three hours.

On uniting the arsenical and verdigris liquids a precipitate is formed which is curdy at first but afterwards slimy, of an insignificant dirty yellow-green shade, which, however, becomes brighter in proportion as the precipitate passes into the crystalline state. This change does not take place within any definite time, considerable fluctuations occurring with even the same temperatures and the same volumes of liquid—*e.g.*, on one occasion in three hours, whilst at another time, under exactly the same conditions, four to five hours are required. In all circumstances it is necessary, in order to obtain a uniform precipitate, that the mixture should be stirred with a long-handled crutch (Fig. 3) until the whole of the verdigris liquid has been run in. This is in most cases essential to secure uniform crystallisation, and consequently an evenly shaded green. The view that the dirty green precipitate is incapable of furnishing well-defined crystals if altered by stirring is quite wrong, and there is no doubt that the omission of a thorough stirring is the cause of an irregular precipitate, the crystals then forming more quickly or slowly, according to the varying fluidity of the strata. This also undoubtedly retards the whole process.

Soon after the stirring of the precipitate has been commenced bubbles of an emerald green colour will form on the surface and increase gradually in number—a sign of internal movement in the mass. At the same time the dirty, dull yellow-green shade changes to a bright green, the precipitate shrinks considerably and settles to the bottom, the top liquor gradually turning blue green. The formation of crystals is now proceeding. After complete rest for about two and a half hours the mass is worked round carefully several times with the crutch, and the remainder of the arsenic solution is run in quickly. Three to four hours afterwards, during which time it is not advisable to stir, the forming process may be regarded as complete. The right moment can be ascertained from a few samples taken out from different parts of the precipitating tank; these when spread out should all exhibit a uniform bright green shade. The mass must be thoroughly stirred again, and left to stand two hours longer. The green settles down closely on the bottom from a clear blue liquid, which is drawn off into the two vats *E* and *F*, where it is treated as described further on.

The resulting emerald green must be washed at least twice with tepid water in the arsenic tank, and then filtered, pressed, and dried.

If in this process the basic verdigris be replaced by the crystallised product, 2 cwt. of the latter are required to 200 lbs. of arsenic, and will yield 175 to 185 lbs. of green—*i.e.*, exactly the same quantity as obtained with the above 154 lbs. of basic verdigris.

In *the new method of manufacturing emerald green* from copper sulphate, arsenic, soda, and vinegar, the charge put in work in the morning must be in the press by the evening of the same day at latest, and with proper management this can be done without any difficulty.

The work must begin in the early morning by charging the arsenic tank (half filled with water at 75° to 80°) with 88 lbs. of (purest) ammonia soda. When the latter has been dissolved by continued stirring, 172 lbs. of white, fine pulverised arsenic are added by degrees, steam being then carefully admitted until (after about four hours) the arsenic is completely dissolved.

Meanwhile the small vat *A* is charged with 206 lbs. of purest copper sulphate, the vat being filled one-quarter full with clear water, and the dissolving effected by the aid of steam. It is a rule that a minimum quantity of water should be used, so as not to unnecessarily increase the volume of the solution by the superfluous introduction of steam. The solution should, however, be thoroughly well stirred.

The hot alkaline solution of arsenic, having clarified somewhat by standing, is run into the working tank as quickly as possible, and is followed at once by the clear, hot solution of copper sulphate (temperature at least 90° C.). Both solutions must be strained through a fine brass sieve. The precipitation product is copper arsenite—a dirty olive-green coloured mass identical with that obtained from verdigris and arsenic, and, indeed, in all cases when soluble cupric salts are treated with arsenious acid (arsenic). The green double salt, copper aceto-arsenite, or emerald green, is formed only by the subsequent action of free acetic acid or its alkaline compounds.

The formation of copper arsenite is accompanied by an active evolution of carbonic acid (from the soda), which is manifested by effervescence, and should be stimulated by careful but not too quick stirring with the crutch. It is, however, impossible to effect the liberation of all the combined carbonic acid by stirring, if only because the stirring must not be continued too long on account of lowering the temperature. In fact, the evolution of carbonic acid continues (though less briskly than at the beginning) through all stages of the formation of emerald green, and generally ceases only with the crystallisation process. This slow liberation of carbonic acid greatly facilitates the regular formation of the green crystals, and is therefore regarded as a favourable sign.

The olive-green precipitate of copper arsenite having been allowed to stand for about ten to twenty minutes, the vinegar can be added. The temperature of the precipitate should not exceed 85° C., nor be less than 82° to 83° C. The length of time the precipitate is left to stand after stirring depends therefore, to some extent on the occurrence of this temperature. To prevent the too violent evolution of carbonic acid the acetic acid must be used in a very dilute condition. Therefore 201 lbs. of acetic acid (60° B.) must be diluted with double that weight of cold water (10° to 12° C.), hot water being added to raise the temperature to 20° to 22° C. Since much depends on quickness in mixing, the discharge tap of the vinegar vat must be large enough to allow the whole to be emptied in two to three minutes. No evolution of carbonic acid should occur during or directly after adding the vinegar, and if such should take place the green will certainly turn out too light in shade. The evolution of carbonic acid should not begin for ten to fifteen minutes, the first indication being a working of the mass in the tank, followed by a sudden foaming of the liquid, and finally by violent effervescence. The mass should now be stirred a short time with care, since this aids incipient crystallisation. When the bubbles cease the mass is left at rest. The dirty green shade hitherto predominant in the precipitate now changes to a brighter green, and after about an hour the formation of the emerald green will be complete. It must be stirred again carefully to convert any copper arsenite adhering to the bottom of the tank to the acetate, and is then left to stand an hour longer. During this time little or no carbonic acid will escape. After another thorough stirring the mass will be found perfectly uniform in shade; nevertheless another hour must be allowed to pass before the blue top liquid can be removed and the washing commenced.

For this purpose the water already placed in the acetic acid or arsenic vat must be boiled. The finished emerald green is then washed twice with the somewhat cooled water, next filtered, pressed, cut into lumps with copper knives, and dried at about 35° C. The sifted material is brought on the market as brand No. 707. The manufactured greens are not all of the same shade, whatever the process used, but vary considerably, sometimes being of a more yellowish, greenish, or bluish shade, according to the more or less perfect formation of the crystals. Hence the freshly manufactured green must always be compared with those already made and added to the stock of the same grade. Certain greens of a coarser crystalline type, and therefore apparently darker, are sold as emerald green No. 808. The production of this kind is, however, purely accidental, there being no reliable recipe for the purpose.

Different brands of emerald green now rarely found on the market, owing their lower price or modified shade to an addition of barytes, gypsum, chromes, &c., can be prepared by mixing pure emerald green with the corresponding material, either directly after the finished green has been washed or in the dry state. In the latter case the mixture cannot, of course, be ground or rolled, but is mixed in a rotary wooden or sheet-iron drum.

To obtain the so-called *parrot greens*, which are now replaced, at least for wall-papers, by certain aniline lakes, which are just as bright and absolutely free from poison, the washed emerald green is treated in the precipitating tank with a cold solution of sugar of lead of varying amount according as a more bluish or yellowish shade is required. This is slowly precipitated with the corresponding quantity of potassium bichromate in cold solution by stirring. It may be washed once with cold water, but this is not absolutely necessary.

The already mentioned mother liquors of emerald green, consisting chiefly of free arsenic, acetic acid, and dissolved emerald green, can be used for making a by-product green known as *soda green*, or green 606, by neutralising the liquors from three batches in the tanks *E* and *F* with a solution of 22 lbs. of ammonia soda, stirred in slowly. This operation must be done in the cold. After the neutralisation, stirring is repeated at the same intervals as mentioned for green 707. The next day the top liquor, now perfectly colourless, is removed, and the green washed at least three times with pure water; then it is filtered, pressed, laid on drying-boards and dried at 35° C. The brighter the emerald from which the mother liquor was obtained, the brighter will these soda greens be; they are almost equal to green No. 707, but somewhat finer in grain.

On neutralising with thin milk of lime, instead of soda, the so-called *lime-arsenic greens* are formed, of a somewhat more bluish shade than the above soda greens, and therefore apparently less bright. On the other hand, they are relatively faster to lime (lime-wash). The collected green liquors are treated with cold thin milk of lime until completely decolorised. The product is not washed, but is filtered directly after precipitation and sufficient settling, and then pressed, dried, and put on the market as lumps or oblong cakes, but very seldom in powder.

Emerald green is used as an oil and water colour. It has only a moderate covering power, but dries well, is very fast to air free from sulphuretted hydrogen. It can be mordanted on fabrics by means of albumin (green tarlatan). Formerly it was largely used for colouring wall-paper, until it was discovered that the putrefaction of the glue and starch paste used for the paper caused a decomposition of the colour, and liberated poisonous arseniuretted hydrogen. Emerald green, like verdigris, is readily soluble in acids and ammonia, and the presence of an insoluble residue always indicates adulteration or the admixture of other substances.

Brunswick Green

This name is at present applied to the Bremen blue already described, but was at one time exclusively used for denoting a very pale and therefore insignificant looking bluish-green pigment, now rarely manufactured.* Nevertheless the method of production being typical for a series of other colours, some of which are much brighter, may be described here. In a small vat, *A* (Fig. 66), 165 lbs. (75 kg.) of Swedish (or other iron-free) copper sulphate is mixed with 55 gals. of hot water and dissolved by steam and continued stirring, followed by an addition of 3¼ lbs. of tartaric acid and reheating.

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* Later on the name Brunswick green was wrongly applied to the far more brilliant emerald green.

The mixture is next run into the precipitating tank, *C*, and diluted here with a three or four-fold quantity of cold water. In an enamelled pan set on a fire 5 ozs. of arsenic are dissolved with ¼ oz. of calcined soda in about 11 galls. of water, the solution being stirred into the solution of copper sulphate in the working tank. Meanwhile a thin milk of lime from 38 to 44 lbs. of quicklime is prepared, and stirred into the copper sulphate solution until complete precipitation results, avoiding, if possible, any excess of lime. The precipitate is allowed to settle down, freed from the perfectly clear top liquid, and washed out twice or three times with cold water. Finally the resulting colour is filtered, pressed, cut into square pieces, and dried at a low temperature. The given weights of raw materials will yield about 130 lbs. of dry colour. For producing lower grades an addition of barytes may be given, but not too much, as the white adjunct has a powerful effect on the originally far from bright colour. The Brunswick green, used formerly very much as a lime colour, has been removed at present by the much cheaper and more intensive ultramarine.

The Brunswick green apparently owes its method of production to the endeavour to imitate *mountain green*, which is probably the oldest green pigment known. This attempt, however, was not successful, for later on products put on the market as "mountain green" contained admixtures of emerald green, besides some ingredients of similar composition to the Brunswick green. The resistance of these colours to lime was thereby, however, considerably lessened, and they gradually went out of use. Still later a certain brand, the so-called Neuwied green, took first place amongst the lime greens, and was also very often called mountain green.

Neuwied Green

This colour, formerly very much in use, especially as a water colour, has at present almost entirely disappeared from the market, as well as its various derivatives, and is only asked for in isolated cases and for special purposes. It is formed of a mixture of emerald green and variable quantities of barytes, gypsum (better qualities being made of blanc fixe), and can be obtained by mixing these materials with the first one in the dry state, as well as by a special wet process. This being similar in principle to the old method of producing emerald green, except for the difference in the proportionate quantities used, the manufacture of Neuwied green can be treated more briefly than the far more important production of emerald green.

The modern recipe for making Neuwied green and producing the brightest shade of this colour is as follows: 110 lbs. of basic verdigris crushed to small lumps must be mixed in the vat *A* (Fig. 66) for about twenty-four hours in 22 galls. of warm water. The mass is stirred until a uniform paste is obtained. Meanwhile 110 lbs. of white, ground arsenic are dissolved in the vat *B*, in the same manner as already described for emerald green, and diluted to 165 galls., 154 lbs. (70 kg.) of finely powdered gypsum are stirred up with warm water and added, through a fine-mesh sieve, to the boiling liquid. The spigots are taken out of *A* and *B* at the same time, and the verdigris liquor allowed to unite with the arsenic solution in the precipitating tub *C*, the whole being well stirred, as well as the contents of the arsenic vat, until the latter is empty. The resulting precipitate of copper aceto-arsenite must be stirred with the crutch until cold. During this operation, and, at all events, before the precipitate gets cold, the barytes, if necessary, can be added in the same manner as the gypsum, being, of course, strained through a hair or brass sieve. The deposited colour must be filtered, pressed, and dried, and is put on the market either in cut pieces of regular size or as a powder.

Another method of producing Neuwied green is similar to that for Brunswick green, and justifies the reputation of this brand of Neuwied green as a lime colour, which is not the case with the Neuwied green obtained by the first process. Neuwied lime green owes its greater brightness and far more greenish tone to the circumstance that a much greater quantity of copper oxide is combined with arsenic. Nevertheless there is no real difference in the two methods of preparation, except that the various recipes prescribe larger or smaller quantities of arsenic for the production of different shades. The fact that an increase of the copper arsenite in the compound lessens the resistance to lime puts a certain limitation on the application of arsenic, and therefore in a certain measure restricts the brightness of the Neuwied green. The following table gives the different weights of the raw materials used according to the best-known recipes:

—	A. Brunswick Green.	B. Neuwied Green.						Imperial Green.
		I.	II.	III.	IV.	V.	VI.	
Copper sulphate . . .	75	75	64	64	64	50	50	105
Potassium tartrate . .	1·5	1·5	—	—	—	—	1·0	—
Arsenic (powdered) . .	0·15	2	12	10	6	5	10	66
Soda (or potash), calcined .	7·5	7–9	—	—	—	50	40	—
Lime, ordinary . . .	17–20	17	8	16	16	—	8	—
Vienna lime	—	—	—	—	—	—	—	21
Barytes	x	20	30	30	30	30	30	50
Gypsum	x	10	—	—	—	10	10	—
Vinegar (6° B.) . . .	—	—	—	—	—	—	—	36

The recipes for Nos. I., V., and VI. are fairly similar to those for producing Brunswick green, with the exception that the quantity of arsenic in the former is relatively much greater. The method of working, too, is the same as for Brunswick green, and therefore need not be repeated.

Nos. II. to IV. inclusive are made without soda (in dissolving the arsenic), so that the several operations, especially the dissolving of the arsenious acid in water, are preferably performed as described for the old emerald green process, whilst the addition of lime is effected according to the Brunswick green method.

The so-called *imperial green*, one of the numberless products owing their existence to more or less advantageously chosen proportions of arsenic, copper sulphate, and vinegar, is a colour sometimes found in the trade. In character, as might easily be guessed from its high content of arsenic, the dull imperial green is neither a decided lime nor an oil colour of any special covering power, and may be regarded as occupying a position between emerald green and Neuwied lime green. The older methods are unsuitable for working on a large scale; only the process based on modern experience will now be described, This colour generally has the same composition as the lime-arsenic green obtained by precipitating the blue liquor of emerald green with milk of lime, only instead of ordinary lime the purer so-called Vienna lime is used, whilst the high content of copper, arsenic, and acetic acid justifies the supposition that a compound similar to emerald green will be obtained. In fact, the best method of making imperial green furnishing a much brighter shade than the obsolete method—is according to the emerald green process, viz., making the copper aceto-arsenite first, and then precipitating the blue top liquor with a solution of Vienna lime until decoloration is complete.

In this precipitation the quantity of milk of lime must be restricted to that exactly necessary for the decoloration of the blue liquor, any excess of lime always dulling the shade of the copper aceto-arsenite, especially on drying. The solution of Vienna lime is prepared, of course, in the same way as with ordinary lime (already described).

According to other instructions, imperial green can be still more simply made by mixing lime-arsenic greens with emerald green in any proportions in the dry state.

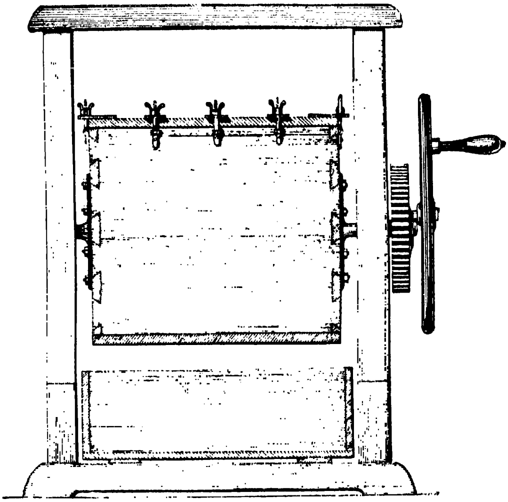
Besides the copper-arsenic greens already described, certain other green copper colours are found in the trade under various names, all of them without exception, however, being merely suitable mixtures of the chief types (emerald, Neuwied, and imperial green), either alone or with barytes. To show this more clearly the best known of these mixtures, as given in older text-books, have been arranged in the following Table. The materials can

Name.	Kirchberger Green.		Mitis Green.			High Green.		New Green.			Jasnig Green.		Paris Green.		Patent Green.		Persian Green.		Parrot Green.			
	I	II	I	II	III	I	II	I	II	III	I	II	I	II	I	II	I	II	I	II	III	IV
Emerald green .	—	—	55	45	35	80	60	20	10	10	30	25	60	50	40	50	75	75	100	100	100	100
Imperial green .	50	40	45	55	65	—	—	40	50	50	70	75	40	50	60	50	45	45	-	—	—	—
Neuwied green .	—	—	-	—	—	—	—	20	20	—	—	—	—	—	—		—	—	—	—	—	—
Barytes . . .	50	60	—	—	—	20	40	20	20	50	—	—	—	—	50	80	20	30	—	20	20	50
Pale chrome yellow, chemically pure .	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	20	10	20	20	10	10

be mixed both by the wet and dry methods. The former method has already been described, so that only the mixing of these colours in the dry state has to be discussed. Apart from their extremely poisonous qualities, the crystalline nature of most of these greens prevents their being ground, sifted, &c., in the way customary for most of the other mineral colours. Thus it is essential that in mixing these colours, alone or with barytes, all dust must be suppressed on account of the safety of the workmen; consequently the apparatus used must be made dust-proof at all lids. doors, slides, joints, dovetails, &c., of boxes, barrels, drums, or the like. The crystalline nature of the copper-arsenic greens, especially of emerald green, precludes any grinding of those colours in mills or edge-runners, since when treated in this way their crystalline structure would be destroyed, and their appearance rendered dull and faded. The avoidance of this disadvantage is, of course, the more necessary on account of the decreased brightness caused by the presence of the white adjuncts. To correct, if possible, this disagreeable result, the coloured mixtures are moistened with cheap hygroscopical saline solutions in the mixing vats (common salt, calcium chloride, &c.), or, more recently, glycerine diluted with an equal bulk of water. This manipulation, primarily intended, of course, to deceive the inexperienced buyer, also considerably reduces the formation of dust, if not preventing it altogether.

The materials are mixed as a rule in drums, or, as balls cannot be used

FIG. 68.

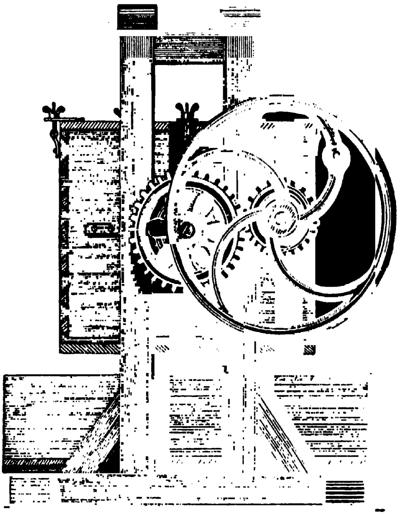


for the reasons already given, preferably in staunch cubical wooden chests fitted with a shaft mounted in a frame and turned by a crank (Figs. 68 and 69).

To secure uniform running, the crank motion is transmitted by pinions. In contrast with the gliding movement of the materials under treatment when mixing drums are used, the cubical shape of the mixing machine causes the motion to be interrupted four times in each revolution, and thus ensures more intimate mixture. The escape of dust can be more securely prevented by lining the chest with sheet zinc. The lid is screwed on with strong wing nuts engaging in hinged forked lugs, and is made dust-proof by a strip of india rubber. When the materials are sufficiently mixed the chest is opened after a short time, during which most of the dust will have settled down. The state of the mixture can be tested by spreading out a sample, and, if satisfactory, the solution of salt for moistening is poured into the colour, the chest being rotated again until a perfectly uniform moistening of the mixture is obtained.

For sifting the pure or mixed emerald green the apparatus shown in Fig. 70 may be used with advantage. It consists in the main of a square sifting frame, a shoot for collecting the sifted colour, and a shaft for the reception of the impurities or coarser crystals that will not pass through the sieve. The whole is enclosed in a dust-tight casing. The materials to be sifted are placed in the hopper, *A*, and are fed by the aid of the revolving three-edged distributor, *B*, on to the sieve, *C*, which is shaken to and fro by the eccentrics, *D*, *E*, and *F*, as can be easily seen from the illustration. From *D* a belt passes over a pulley on the extension of the shaft of the three-edged distributor, *B*, which is thereby made to revolve. The sifted materials fall through the shoot *G*, and into a barrel underneath. Particles that will not pass through the sieve run down through the slit *H* into the shoot *J*, and are collected by a barrel placed below. To facilitate the conveyance of the barrels without disseminating dust, they may be mounted on small flat trucks running on rails extending right under the apparatus.

FIG. 69.



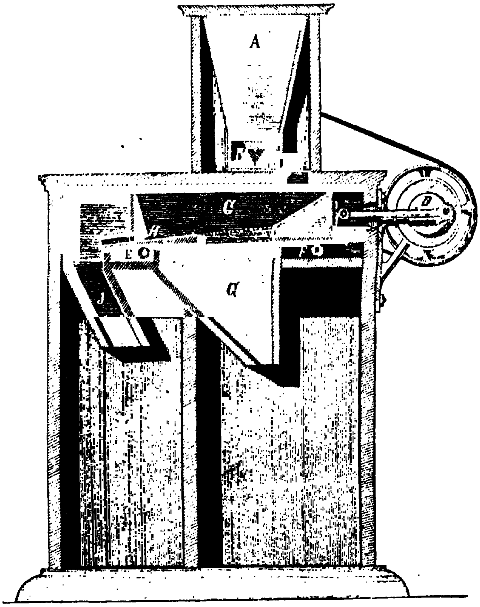
This apparatus, though suitable only for crystalline colours, works admirably if properly managed. It can be recommended for sifting emerald green, if only for the reason that it prevents any dissemination of dust. The machine can be worked by hand if no other source of power is available, and in such case the driving pulley, *D*, must be provided with a crank and a flywheel.

Arsenic Disease

Arsenic is the strongest mineral poison known. It affects not only the animal organism, but plant life as well. This poisonous action is not confined to white arsenic (arsenious acid), but extends to all other arsenic compounds also, and is the greater in proportion to their solubility in water. For arsenic poisoning to occur it is not essential that the arsenic should enter the human system through the digestive organs, but poison may enter by inhaling gases, vapours, or dust containing arsenic, by repeated contact with the skin, by the contamination of open wounds, &c., and the case may be acute (even suddenly fatal) or chronic and of gradual development.

In all acute cases the symptoms immediately appear in the stomach and intestines, which are inflamed and destroyed, the pulse becoming rapid and fluctuating. Next come violent pains, convulsions, trembling, muscular weakness, and fainting. The arsenic enters the blood very quickly, and can be detected with certainty after death even when the bodies have been buried years, since they remain in a good state of preservation for a remarkably long space of time mummified by this poison.

FIG. 70.



As a trade disease, chronic arsenical poisoning is a risk incurred by all persons who are continually occupied with arsenic compounds *e.g.*, men engaged in works where these compounds are prepared, and miners (arsenical fumes, recovering silver from lead ores, &c.). Stomach-ache, a tendency to vomit, and violent thirst are the first symptoms, followed in the later stages by inflammation of the stomach and the intestines, jaundice, diarrhœa, succeeded by constipation, cough, salivation. The hair and nails become loose, the skin is covered with pustules and sores, the body becomes lean and seems to shrivel up. Insomnia, weariness, and lameness ensue, finally ending in death. The treatment of chronic arsenic poisoning—after the dangerous occupation has been abandoned—consists in administering easily digestible, invigorating, slimy, mealy, and fatty nourishment of a concentrated character. Sulphur baths must also be taken. In acute cases artificial vomiting must be produced, and the stomach being freed in this way from its poisonous contents, the arsenical antidote must then be administered, consisting of a freshly prepared warm mixture of the hydroxides of iron and magnesium. This is also used, too, for rubbing the skin or bathing, if the poison arises from external causes. Purgatives must be taken until the ferric hydroxide passes away in the fæces; and wines, coffee, tea, &c., in copious quantities are prescribed as stimulants.*

For the sake of completeness, the production of certain other green copper colours, which, though not at present produced to the same extent as was formerly the case, still possess a certain amount of interest, will now be mentioned. These are the so-called *Scheele's green* and *Elsner green.*

Scheele's green is the name given to two quite different commercial products. The method of producing the real Scheele's green was discovered by C. W. Scheele, 1742–86, a native German chemist domiciled in Sweden, who was the first to manufacture this product. From Sweden it was introduced into Germany, and was probably soon imitated by a different process, the original method having been kept a strict secret, according to the custom of the time. This may be the reason why in Germany an entirely different product was put on the market as Scheele's green.

As a pigment it is no longer used in England.

The *real Scheele's green* is almost the only green copper colour which can be manufactured in the pure state in a whole range of tones from the palest to the darkest green. The prime factor is the content of arsenious acid, the different grades becoming the paler—viz., yellower—the larger the quantity of arsenic present in the compound. The manufacture of this green differs from the methods already described for copper-arsenic green, caustic potash or soda being used instead of lime. These materials are easily purchased, and can also be made in colour works by treating caustic lime with potash (potassium carbonate) or soda at boiling heat, according to the equation

$$\underbrace{Ca(OH)_2}_{\text{Caustic lime (slaked lime)}} + \underbrace{Na_2CO_3}_{\text{Soda}} = \underbrace{2NaOH}_{\text{Caustic soda}} + \underbrace{CaCO_3}_{\text{Calcium carbonate.}}.$$

Besides the caustic alkali a corresponding quantity of insoluble calcium carbonate is obtained, and this settles down to the bottom in the form of a white precipitate, thus enabling the alkali to be separated very easily. A certain quantity of freshly slaked lime is put in an iron pan, thinned down with water, and treated with a calculated amount of soda (dissolved in a little hot water), the whole being then heated with constant stirring until it boils. This temperature is maintained until the chemical reaction is complete, or at least only a small excess of undecomposed soda is left. An insufficiency of soda for combining with the lime must be avoided, since any excess of lime will lighten the shade of the green—a risk that is not incurred with an excess of soda or potash. The reaction being finished, the colour is allowed to settle down and the clear top liquor siphoned off into a special (iron) vessel. The residue in the pan is washed twice with clean warm water. The two clarified washings are united to the siphoned liquor, which, after stirring up thoroughly to obtain uniform concentration, is ready for use. The residue of calcium carbonate in the pan is generally useless.

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* The German laws do not deal especially with the danger of constantly working with arsenic compounds, but prescribe the necessary appliances and methods of working.

In making Scheele's green a vat as illustrated in Fig. 1, and containing about 550 to 660 galls., is required. This must be filled about half full with cold water. A hot solution of ¾ cwt. of copper sulphate in about 110 galls. of water is poured in. 35 lbs. of calcined soda and 11 to 30 lbs. of arsenic—according to the shade desired—are dissolved in a fivefold quantity of water in a separate copper pan, the solution being allowed to clarify. The alkaline solution of arsenic obtained in this manner is stirred up in the working tank with the copper sulphate solution. This mixture is treated with the cooled solution of potash or soda until no more copper can be detected in the filtrate from the resulting green precipitate. Stirring must be continued a short time, and then the colour is allowed to settle down, after which it is washed several times with cold water before being filtered and pressed. The pressed colour, cut into oblong pieces, is dried in the same way as the other copper-arsenic greens. Scheele's green, however, is said to become considerably brighter if it be exposed (after drying) to a temperature of 60° to 70° C. for some time.

The genuine Scheele's green has a conchoidal fracture and a lustrous surface. The greater this lustre, the darker is the shade of the green, this property being a criterion of the commercial value, whereas the brightness is impaired by white admixtures, such as barytes, gypsum, &c. Scheele's green is put on the market almost exclusively in a perfectly pure state. A small addition of potassium zincate increases the lustre of the product.

Another pigment, often known under the same name, is obtained by precipitating a solution of dilute copper sulphate with an alkaline solution of arsenic. The operation is performed in a tank of the same size as that used for the genuine Scheele's green. 2 cwt. of iron-free copper sulphate and 200 lbs. of calcined potash or soda are used, and these are dissolved, together with 33 to 66 lbs. of arsenic. This colour too must be washed several times to obtain a good product. The colour is of fairly good covering power, and can be used as water and oil colour, as well as for lime-wash.

The so-called *Elsner green* is still sometimes used for painting in oil. From its character this colour must be considered as belonging to the lakes, its preponderating content of copper hydroxide being the sole reason for classing it here with the green pigments. Elsner green consists of a mixture of Bremen blue and a fustic-tin lake, and can be obtained by direct precipitation or by simply mixing the above-mentioned finished products.

In the former case a solution of copper sulphate is diluted with a quantity of an aqueous extract of fustic, 10 to 12 per cent. of tin salt dissolved in water being added, and the mixture precipitated with caustic soda or potash until the copper solution is completely exhausted. The precipitate having settled down, the limpid top liquor is removed, and the pasty residue is re-blued by adding caustic soda. The mass is next washed quickly and repeatedly with cold water. The filtered and pressed colour must be dried at a low temperature (30° C.). The larger the quantity of fustic used, the greener will be the shade of the colour.

In the other method of preparation freshly prepared and well washed Bremen blue is mixed with a liquid fustic lake (*q.v.*) in any convenient proportion, filtered, pressed, and dried at a moderate temperature.

Though Elsner green is sometimes put on the market as "non-poisonous," this is, of course, inaccurate, since even in absence of arsenic it contains poisonous copper salts.

The following additional green copper colours may be mentioned, even though they have no practical value:

Casselmann's green is a compound of copper sulphate with copper hydroxide, and has a markedly bright shade.

Kuhlmann's green is basic copper chloride, and greatly resembles emerald green in effect. It is more durable and cheaper than the latter, and has the property of retaining its pure green shade under artificial illumination.

Boron-copper green is copper borate. It will stand the strongest heat, and is therefore used as a ceramic colour. The tone can undergo modification according to the kiln temperature used.

Copper silicate, obtained by precipitating a solution of copper with water-glass (alkali silicate), will also stand high temperatures. This compound is said to have been known to the old Egyptians, and is therefore called *Egyptian green.*

Gentele's green is cupric stannate.

b. Chrome Oxide Greens

Chromic Oxide, Cr_2O_3.—In view of the superior qualities of chromic oxide, its perfect fastness to light and indifference to chemical and thermal influences of all kinds, this compound might be regarded as one of the most ideal colours for technical purposes. Unfortunately, however, it fulfils to only a limited extent the other requirements exacted of a perfect pigment. Although chromic oxide can be made of sufficient brightness, it gives, when ground in the manner necessary for paints, merely a grey-green powder of very low brightness and covering power. On the other hand, chromic oxide improves in brightness when used with oil, and therefore might form a suitable pigment for certain purposes were it not that the extremely high price of the raw materials precludes its use in many instances. A number of cheaper methods are known, but none of them will furnish a product of universal technical use. Hence the application of chromic oxide is limited to certain graphical purposes (bank-notes, bonds, &c.), as well as for artist's colours and porcelain painting, for which its high price is of no importance.

It is quite another thing, however, with regard to the *chromium hydroxides.* The most important representative of this group—viz., *Guignet's green*—not only embodies the superior qualities of chromic oxide (besides being superior in brightness), but can also be produced by a process which enables this cheaper product to be used in paints. However, to utilise the superior qualities of chromium hydroxide green for ordinary paint it must be mixed in suitable proportions with some pigments of good covering power. This also enables different shades to be obtained. For this purpose the different kinds of chromate yellows,- and amongst these more especially zinc chrome, are most suitable. However, by mixing chromium hydroxide with this pigment new colours, the so-called *permanent* or *Victoria greens,* are obtained, which no longer have the superior properties of pure Guignet's green, but exhibit, in a certain degree, the sensitiveness of zinc chrome.

The fastness to light, however, remains unimpaired, owing to the absolute fastness of the zinc chrome. The resistance to the caustic action of lime, which has to be considered in the case of ordinary paints, is only slightly diminished. The case is, however, different with regard to resistance against acids. Zinc chrome, being already somewhat soluble in water, cannot resist dilute acids; and the same applies to lead chromates, which are completely soluble in hydrochloric acid, whilst with sulphuric and nitric acid they form dirty-looking compounds. Paints made from mixed chromic oxide green pigments are therefore unsuitable for use where they may be exposed to the influence of acids, even in the form of weak acid vapours. The fact of these paints being made with oil, and even covered with a layer of copal varnish, makes no difference, since both these vehicles are unable to stand the influence of acids.

Pure chromic oxide green being produced at a low red heat—between 500° and 700°—can be used with a fire-proof vehicle for paints to stand high temperatures, though above 800° chromium hydroxide turns to a dirty brown shade. This behaviour toward high temperatures is considerably modified in permanent greens. With light shades a temperature of not quite 200° C., and with dark shades, in which chromic oxide is predominant, 400° C., will be sufficient to destroy the brilliancy of the paints. Nevertheless iron articles exposed to a temperature up to 200° C. can be painted with permanent green without risk. This fact is actually utilised in practice in painting locomotives, motor-cars, &c.

The raw materials for producing chromic oxide (Cr_2O_3), as well as for Guignet's green (chromium tetrahydroxide, $Cr_2O(OH)_4$), are especially potassium bichromate (bichromate of potash, $K_2Cr_2O_7$), and of late the corresponding sodium salt. We will now briefly describe several processes by which chromic oxide can still be profitably manufactured on the large scale, in order to mention the chief features of this very interesting colour, and also to elucidate the manufacture and properties of the still more important chromium hydroxides.

According to *Wöhler,* chromium oxide can be obtained by heating a mixture of yellow (neutral) potassium chromate, K_2CrO_4, and ammonium chloride (NH_4Cl). In washing the fused product with water, potassium chloride passes into solution, while chromium oxide remains as a dark grass-green coloured mass. This chemical reaction is typical of a large number of technical methods of manufacturing chromium oxides. Instead of the neutral potassium chromate, however, the more easily obtainable potassium bichromate is used.

The brightest chromium oxide is obtained by heating mercurous chromate or ammonium bichromate. In the former case the mercurous chromate is decomposed at high temperature to chromium oxide, oxygen, and metallic mercury, while ammonium bichromate is decomposed by heat into chromium oxide, water, and nitrogen.

$$\underbrace{(NH_4)_2Cr_2O_7}_{\text{Potassium bichromate}} = \underbrace{Cr_2O_3}_{\text{Chromium oxide}} + \underbrace{4H_2O}_{\text{Water}} + \underbrace{N_2}_{\text{Nitrogen.}}$$

Unfortunately these two methods are far too expensive for technical use, and therefore possess merely a theoretical interest. Hence in practice use is preferably made of methods similar to those introduced by Wöhler, by melting potassium chromate with ammonium chloride. As already mentioned, the potassium bichromate, or sodium bichromate, is almost exclusively used as the raw material, while ammonium chloride can be replaced by cheaper materials, such as carbon, sulphur, gypsum, &c. The chemical reaction occurring with the different reducing agents can be explained by the following equations:

1. In reducing with sulphur:

$$\underbrace{K_2Cr_2O_7}_{\text{Potassium bichromate}} + \underbrace{S}_{\text{Sulphur}} = \underbrace{Cr_2O_3}_{\text{Chromium oxide}} + \underbrace{K_2SO_4}_{\text{Potassium sulphate.}}$$

2. In reducing with carbon:

$$\underbrace{K_2Cr_2O_7}_{\text{Potassium bichromate}} + \underbrace{2C}_{\text{Carbon}} = \underbrace{Cr_2O_3}_{\text{Chromium oxide}} + \underbrace{K_2CO_3}_{\text{Potassium carbonate}} + \underbrace{CO}_{\text{Carbon monoxide.}}$$

3. In reducing with ammonium chloride:

$$\underbrace{K_2Cr_2O_7}_{\text{Potassium bichromate}} + \underbrace{2NH_4Cl}_{\text{Ammonium chloride}} = \underbrace{Cr_2O_3}_{\text{Chromium oxide}} + \underbrace{2KCl}_{\text{Potassium chloride}} + \underbrace{4H_2O}_{\text{Water}} + \underbrace{2N}_{\text{Nitrogen.}}$$

4. On decomposition with gypsum ($CaSO_4$):

$$\underbrace{K_2Cr_2O_7}_{\text{Potassium bichromate}} + \underbrace{CaSO_4}_{\text{Gypsum}} = \underbrace{Cr_2O_3}_{\text{Chromium oxide}} + \underbrace{K_2SO_4}_{\text{Potassium sulphate}} + \underbrace{CaO}_{\text{Calcium oxide}} + \underbrace{3O}_{\text{Oxygen.}}$$

As may be seen from the first three equations, the soluble potassium salt, corresponding to the reducing agent, is always formed, in addition to chromium oxide, and can be removed more or less easily by leaching the fused product with water. In Equation 4, in addition to potassium sulphate, calcium oxide is formed, on which account the washing of the fused product cannot be effected with water, and must be carried out with dilute hydrochloric acid, to prevent the re-formation of gypsum, which would then remain mixed with the chromium oxide.

The reduction process can be technically carried on in large covered Hessian crucibles, exposed to a strong red heat in suitable furnaces, or in closed retorts (Figs. 71 and 72). Care must be taken to ensure the proper removal of the resulting gases, oxygen, carbon monoxide, &c. As is the case with all products obtained by heating, the raw materials must be used in the finest possible state of division. The mixing of the weighed raw materials is best performed in an edge-runner mill. When larger quantities are being treated the mixture can then be run through a stone or beating mill. Here the heating of the mixture in the mill must be carefully prevented, especially when the reduction is to be effected by sulphur. The following proportions will give specially good results :

1. 2 parts potassium bichromate to 1 part sulphur.
2. 5 „ „ „ „ 1 „ sublimed sulphur.
3. 4 „ „ „ „ 1 „ „ „
4. 3 „ „ „ „ 1 „ carbon (soft charcoal).*
5. 3 „ „ „ „ 1 „ sal ammoniac.
6. 1 part „ „ „ 3 parts gypsum.
7. 240 parts „ „ „ 32 „ carbon, 10 parts saltpetre, 5 parts sulphur, and 5 parts sal ammoniac.†

Whilst, as already mentioned, the mixtures 1 to 6 must be exposed to a strong red heat in closed retorts, the mixture 7, after being intimately mixed, must be piled up in conical heaps on the sole of a reverberatory furnace. These are then ignited, and the resulting residue is heated again at a low red heat. In this case, as in all others, the fused product forms a spongy, blistered, hard mass, which must first be crushed in edge-runners, screw or beating mills before leaching is practicable. This latter operation is performed in tanks. The coarse-grained, pulverised residue is boiled with water, by direct steam, until the soluble salts are all extracted, which in some cases may take a considerable time. The undissolved residue must then be left to settle down, and the generally useless top liquor removed by decantation. The residue is allowed to drain in filter boxes, similar to those shown in Fig. 62, or some other corresponding device. Here, if necessary, the mass may be re-washed with hot water. The fused product from mixture No. 6 containing some calcium oxide, besides potassium sulphate, must be treated with very dilute hydrochloric acid, and the residue washed once by the aid of steam.

The chromium oxide, washed in this manner, must be well dried, after pressing, and recalcined for some time at a low red heat.

Care must always be taken that the mixture contains as little iron as possible, since this metal makes the already poor shades of chromium oxide pigments still duller, owing to the formation of iron oxide, or the black sulphide of iron. Any existing compounds of iron can be easily removed by digesting the leached fused products with dilute hydrochloric acid. If the sulphide of iron is formed owing to the presence of sulphur in the mass, a more or less brisk evolution of sulphuretted hydrogen gas will occur on adding the hydrochloric acid. In any case, even when boiling is resorted to, the iron oxide dissolves very slowly in the dilute acid.

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* Instead of soft wood charcoal potato starch can be used, or paper-maker's wood-pulp (cellulose), extracted with hydrochloric acid, or other materials furnishing pure carbon when heated.

† According to Ludwig.

When this digestion is finished the dissolved iron salts must be thoroughly washed out of the mass.

Mention is frequently made in the technical press of methods for producing chromium oxide in the wet way. Such instructions are rarely successful in practice, since the resulting chromium oxide (apart from the one obtained by precipitating a solution of chrome-alum with soda and heating the resulting chromium hydroxide) is not nearly so bright as that made by the dry method.

Casthelaz and *Leune* (*Dingler's Journal*, cxc., p. 429) obtain chromium oxide of more beautiful and purer shade than Guignet's green (?) by precipitating a chrome solution very slowly with insoluble or sparingly soluble hydroxides, hydrated metallic carbonates, metallic sulphides, and other combinations of weak acids. The process is said to give very regular results. The same object is said to be attained by immersion in slightly acidified solutions of chrome, metals (such as iron or zinc) exhibiting an affinity for the acids of chromium salts. According to the statement of the inventor, the solution of any chromium salt (chromium chloride, chromium sulphate, chrome alum, &c.) is converted into the grey modification by boiling or other means (unless this state has already been attained). The solution, cooled down to 8° to 10°, is gradually treated with gelatinous alumina (or zinc hydrate, zinc carbonate, freshly prepared zinc sulphide, metallic iron or zinc, &c.), whereupon chromium oxide will quickly be formed, especially if the temperature be raised to boiling-point. This product merely requires washing to attain a state suitable for all technical requirements. If the precipitating agent is a body that forms insoluble compounds with the acid of the chromium salt, the shade of the chromium oxide will naturally be correspondingly impaired.

Chromium oxide is a dark grass-green powder, perfectly insoluble in water and nearly all acids. It is infusible, and imparts a pretty green tinge to glasses. Upon this quality rests its application in the pottery and glass industries, as well as (more especially) for porcelain painting. It is used, too, as an artist's colour, in the graphic arts and for fireproof paints. It has also a small sale for the manufacture of sealing-wax. Chromium oxide is largely used in addition to the chromium hydroxide, described in the following section, in calico printing.

True Chrome Green, Guignet's Green (*Smaragd Grün, Vert de Guignet*)

On account of its superior qualities, the chromium tetrahydroxide, of the formula $Cr_2O(OH)_4$, has a larger technical application as a pigment than any of the others. Its preparation from potassium bichromate and crystallised boric acid, although already known for a long time, was first made public by *Guignet*, from whom the colour derives its name, *Guignet's green*. The process is still the same as described by the inventor, the only modifications made being confined to the improved construction of the furnaces where the calcining process takes place, in order that a portion at least of the valuable boric acid lost by sublimation * may be recovered. This has been made possible by the employment of muffle and retort furnaces provided with a suitable system of flues for condensing the volatilised boric acid.

The chemical reaction in the formation of chromium tetrahydroxide by calcining a mixture of potassium bichromate and boric acid at a dull red heat can be theoretically explained as follows: As the charge fuses, water and oxygen are liberated, and chromium borate and potassium are formed, the latter passing into solution on leaching the fused product with water. The chromium borate is decomposed by this treatment with water to chromium tetrahydroxide and boric acid. The reaction is expressed by the following equations :

1. Heating process :

$$\underbrace{K_2Cr_2O_7}_{\text{Potassium bichromate}} + \underbrace{16B(OH)_3}_{\text{Boric acid}} = \underbrace{Cr_2(B_4O_7)_3}_{\text{Chromium borate}}$$

$$+ \underbrace{K_2B_4O_7}_{\text{Potassium borate}} + \underbrace{24H_2O}_{\text{Water}} + \underbrace{3O}_{\text{Oxygen.}}$$

2. Decomposing with water :

$$\underbrace{Cr_2(B_4O_7)_3}_{\text{Chromium borate}} + \underbrace{20H_2O}_{\text{Water}} = \underbrace{Cr_2O(OH)_4}_{\text{Chromium tetrahydroxide}} + \underbrace{12B(OH)_3}_{\text{Boric acid.}}$$

Although according to the above formula 16 molecules of boric acid should be sufficient for the decomposition of 1 molecule of potassium bichromate, much greater quantities are used in practice to obtain a favourable result. This excess of boric acid plays a special part in the process of forming chromium borate, for although it apparently does not enter into the reaction at all, but only sublimes during the calcination, its presence seems essential to the successful production of bright Guignet's green. The explanation is afforded by the mechanical part played by this portion of the boric acid in introducing and regulating the process of calcination, experience showing that the charge becomes more sensitive to the predominant high temperature when the sublimation of the free boric acid has terminated, a moment that usually coincides with the satisfactory completion of the heating process itself. In all cases where, after the volatilisation of the free boric acid, the heating of the mass is continued the temperature in the retort seems to increase out of all proportion, thus augmenting the risk of forming the dreaded rust stains (brownish to blackish places) in the otherwise beautiful emerald-coloured product. This phenomenon appears if the excess of boric acid is lessened or avoided, from a false notion of economy by the inexperienced. In such case the heating process, even when carried out with the greatest care, often results in a brownish mass, the yield being also far lower than usual. Even

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* We have retained this expression as being used in practice, though, as a matter of fact, crystallised boric acid does not sublime, but volatilises from aqueous solutions along with considerable quantities of steam.

during the heating process—an amount that can be calculated exactly—and secondly on the rate at which the heating process is carried on.

Another point revealed by this circumstance is the mistake committed by moistening the charge, as is sometimes recommended, since it increases the amount of water, and consequently a loss of boric acid.

The manufacture of Guignet's green is therefore divided into three stages: mixing the raw materials, heating this mixture, and treating the calcination product with water.

The first stage proceeds in the usual manner, by mixing the raw materials in edge-runner mills, and then grinding them between millstones. The most favourable proportions to use are: 1 part, by weight, of potassium bichromate to 3 parts of crystallised boric acid, the mixing being, of course, considerably facilitated by using the former in the state of fine powder.

As already mentioned, the heating process is nowadays conducted exclusively in earthenware or cast-iron retorts, of which about four can be set up in one furnace. Figs. 71 and 72 represent such a furnace in elevation and longitudinal section. Furnaces of a simpler construction may be used, according to the size of works, especially if the loss of boric acid by volatilisation with the steam be disregarded. In such event very favourable results are obtained with any kind of retort stove that is provided with a sufficient draught and is carefully supervised. In no case, however, may this furnace be used for any other purpose.

The arrangement of the retort stove shown in Figs. 71 and 72 will be intelligible from the sketch. The retorts are built up of earthenware plates or composed of muffle-shaped fire-clay tube sections of large diameter, and are put in the furnace in such a way that their surface is exposed to the heat on all sides. At the front end of the furnace where the fire-grate is situated the retorts project a little beyond the wall of the furnace, and are fitted here with strong cast-iron doors, the iron connections for the flues serving to condense the escaping boric acid. The latter device communicates with all the retorts in common, and discharges outside the furnace into a single pipe, which leads the condensed liquid into a wooden or iron receiver. The doors of the retorts are provided with round peep-holes.

The retorts are charged when already at a dark red heat, for reasons easy to understand in view of the behaviour of the boric acid as already explained. Soon after the retorts have been charged and closed the reaction begins. The finely ground mass, being very loose, collapses at first on account of the decomposition of the boric acid and the escape of the water of crystallisation. It then softens and intumesces to a spongy mass. This indicates the stage of the reaction explained by Equation 1 on page 233, viz., the incipient formation of chromium borate, the bubbles being caused by the escaping steam and expelled oxygen. This reaction progresses as the dull red heat of the retorts is maintained, and will be complete when the whole mass is red hot. There is no advantage in leaving the product in the retorts any longer, so the nearly soft mass is raked out with long iron crutches into sheet-iron boxes underneath, where it gradually cools, and assumes a bright dark emerald green shade. The resulting chromium borate retains its spongy appearance when cold, but becomes very hard. It is remarkably light, the more so in proportion as the reaction has proceeded satisfactorily.

Immediately the retorts are emptied a second charge is put in, and so forth. The suitable amount of the charge in each case depends naturally on the dimensions of the retort, and must be ascertained by experiment. It must, however, be borne in mind that large charges, though they might economise fuel, would not only endanger the successful course of the heating process, but also make the work of charging and emptying the retorts unnecessarily difficult. It is therefore advisable to make the individual charges too small rather than too large, since, on account of the high price of the raw materials, the risk of spoiling a batch far outweighs the small saving of fuel.

If the chromium borate were left too long in the furnace after the reaction is over, or if the temperature were allowed to rise too high during the reaction, then the aforesaid rust stains would appear and the mass would fuse, especially at the surface of contact with the bed of the retort. This would entail injury to the retorts, in addition to a loss of material. In these circumstances the boric acid—deprived of the whole of its water by the great heat and converted into boron trioxide, B_2O_3—combines with the simultaneously produced chromium oxide to form an extremely hard glass, which in the molten state covers the bed of the retort, and can only be removed with great difficulty when cold. If such accidents be repeated the retorts will soon become useless, or at any rate require an increased consumption of fuel to heat them up to redness.

The next stage is the decomposing of the resulting chromium tetrahydroxide (the true Guignet's green) and boric acid by means of water. This operation is delayed until considerable quantities of the melt have been collected, the reason being twofold. In the first place, the treatment of a large quantity at a time saves labour, and as hot water or steam is needed there is also a saving of fuel. The second, and still more important reason, however, is that more highly concentrated liquids are obtained. As already mentioned, the treatment of chromium borate with hot water furnishes solutions containing calcium borate (formed in the heating process), together with free boric acid, in such quantities that it becomes profitable to recover these products in a suitable form for use over again. The only way to do this being to evaporate the solutions until crystals are deposited, it is easy to understand that this operation can be greatly facilitated and cheapened by obtaining highly concentrated liquids at the outset. For this reason the process of decomposing the calcined product must be carried on with a minimum of water, which can only be done by using steam.

The principle of the arrangement used for this purpose has already been described—for instance, in the process of dissolving lead in vinegar. In this case, too, a large wooden tank, with false bottom, is preferably used. The false bottom is arranged at about one-fifth of the height of the tank, but can easily be taken out and, if necessary, placed at a higher or lower level. This false bottom is perforated with a considerable number of holes of about the size of a pea. The walls of the space between the two bottoms are provided with two diametrically opposite openings at different levels, the higher being connected with a steam pipe, whilst the other serves for discharging the resulting solutions, and is fitted with a tap or spigot. The outlet opening must be placed close against the solid bottom of the tank, and the latter arranged in such a position that the liquids can run off into vessels underneath. Since the solutions must be afterwards treated with hydrochloric acid to convert the calcium borate into boric acid, it will be advisable to have two tanks, one above the other. The upper one, provided with a false bottom, serves for the decomposition of the chromium borate by steam, and the lower one for the hydrochloric acid. If this arrangement is precluded from lack of space, the tanks must be placed side by side in such a way that the liquids from the dissolving tank can be easily transferred to the decomposing tank. The former tank must, of course, be provided with a close-fitting cover of boards.

The false bottom having been put in place, the upper part of the tank is filled to the top with chromium borate, which need not be crushed. The lid is put on, and a gentle flow of steam is admitted. The melt is decomposed at once by contact with the steam, the action being accelerated by gradually increasing the flow of steam. Under this treatment the product changes completely, the shade becoming lighter and brighter. The hard chromium borate is converted into the pasty chromium tetrahydroxide, which can easily be pulverised when dry, and forms the commercial Guignet's green. The admission of steam is continued until a sample of the green shaken up with hot distilled water cedes merely traces of potassium borate to the latter. This can be tested by evaporating a filtered sample of the washings on platinum foil, whereupon nothing but a very small residue should remain.

When the withdrawal of the solutions from the dissolving tank into the decomposing tank has been continued for some time—in the course of which operation a small quantity of the green is unavoidably carried with the liquid—the first tank is opened, and the false bottom is swilled with hot water and taken out of the tank, which is then filled to the top with hot water. After a thorough stirring the mixture is allowed to settle down. The washing water, which is of no value, is renewed two or three times if necessary, though it is apparently impossible to extract the whole of the boric acid in this manner, for Guignet's green, even after the most careful washing out, still contains some traces of boric acid. The colour paste, when sufficiently washed, is then filtered, pressed, and dried in the usual manner.

The solution in the second tank chiefly contains potassium borate, $K_2B_4O_7$, with variable quantities of free boric acid. It is treated with an excess of technical hydrochloric acid, when sufficient volume of the liquor has accumulated. This converts the potassium borate into potassium chloride and boric acid, H_3BO_3, the free boric acid being also precipitated. The above reaction proceeds according to the following equation:

$$\underbrace{K_2B_4O_7}_{\text{Potassium borate}} + \underbrace{2HCl}_{\text{Hydrochloric acid}} + \underbrace{5H_2O}_{\text{Water}} = \underbrace{4H_3BO_3}_{\text{Boric acid}} + \underbrace{2KCl}_{\text{Potassium chloride.}}$$

However, for the process to be of practical use it is necessary that the solution should be sufficiently concentrated, and therefore the liquids, if very dilute, must be concentrated before they can be treated with hydrochloric acid. The precipitated boric acid must be separated from the solution by filtration, and is dried on wicker frames covered with cloth, at a moderate temperature. The residual solution, containing potassium chloride, is thrown away unless some other use can be found for it. When carefully supervised, the recovery of the boric acid will prove a source of considerable profit.

The liquid boric acid draining from the condensing flues of the furnaces into the receiver provided for the purpose is placed in the decomposing vat for treatment with the solution from the chromium borate.

Instead of potassium bichromate, the cheaper sodium bichromate can be used for producing Guignet's green without any alteration of the manufacturing process, but the yield obtained is somewhat less than when the potassium salt is used, and the product is generally of a lighter shade. If the process has been well managed, 100 parts of potassium or sodium bichromate will yield 63 to 65 parts of Guignet's green, according to the content of boric acid in the latter.

In a pure state Guignet's green has a very bright dark emerald green shade. It is not only perfectly fast to air and light, but, if properly made, will also resist the influence of alkalies and most mineral acids. When fused with saltpetre on platinum foil or in a porcelain crucible it is converted into potassium chromate, a reaction common to all chromium oxides, and serving as a test for these oxides. Guignet's green, heated above its temperature of formation, loses its bright appearance in a short time, parting with its water of hydration and changing into the duller chromium oxide. Pure Guignet's green is mostly used in calico printing, for wall-papers, bank-note printing, chromo-lithography, &c.—*i.e.*, for all purposes where its fastness is the determining factor.

Sometimes Guignet's green is made by heating potassium bichromate with arsenious acid, a method giving products which are brighter than that obtained with boric acid, but very poisonous. The colours are also known in the trade as *emerald* or *Victoria green*. True Guignet's green is also required and sold in some countries as Victoria green. On the other hand, the name *Mittler's green*, applied to Guignet's green, is now very seldom used.

Other Chromium Oxide Greens

(*Plessy's Green, Arnaudon's Green, Schnitzer's Green, Dingler's Green, Casali's Green*)

All other chromium oxide pigments are far inferior in intensity and brightness to Guignet's green, and, independently of their very high cost of production, have not yet succeeded in making any headway in practice. The reason why, in spite of this, we devote a little space to mentioning these chromium oxide compounds is because there seems to be an opportunity of preparing these green pigments by known manufacturing processes and of obtaining products of considerable interest to the consumer. To make these colours available for practical use the first essential is to reduce the high prime cost to a level in consonance with their appearance and other properties, with special regard to their fastness to thermal and other influences. The chief obstacle seems to be caused by the necessity for using the expensive bichromates; for whilst the chromic acid colours, such as chromes, zinc chrome, chrome red, &c., give results corresponding to a loss of barely 30 per cent. of the weight of the raw materials, the loss in the case of the chromium oxide pigments cannot be estimated at less than 50 per cent.;

and, indeed, a still greater loss is experienced in making pure chromium oxide by the reduction of bichromate. Now the possibility of combining chromium oxide with phosphoric acid, and thereby obtaining a higher yield in conjunction with a lower cost price, is proved by the existence of the numerous combinations mentioned at the head of the present subsection, all of which are chromium phosphates, so far as concerns their most essential ingredient. It is also justifiable to assume that still more advantageous results could be obtained by following the matter up in a scientific and technical manner.

With regard to the above-mentioned colours, *Plessy's green* undoubtedly deserves special consideration, the method of production being cheaper and more feasible than that of Arnaudon's and Schnitzer's green, as well as apparently susceptible of considerable improvements. The Plessy process consists in treating a solution of bichromate with calcium biphosphate and cane sugar as reducing agent, and is briefly as follows:

Twenty-two pounds of potassium bichromate are dissolved in about 22 galls. of hot water, and the solution is firstly treated with 6½ galls. of calcium phosphate solution containing 6·5 per cent. of phosphoric acid, and afterwards with 11 pounds of cane sugar. After a short time a considerable evolution of gas occurs, causing such a violent effervescence that it must be moderated from time to time by diluting the liquid with water to prevent frothing over. The reducing action of the sugar takes about twenty-four hours, after which time the green colour will be fully formed. The colour settles down completely to the bottom of the vessel, and the clear top liquid is then poured off. The green is washed two or three times with clear water, and is then filtered, pressed, and dried.

The calcium phosphate solution is prepared by treating white calcined bones for a long time with hydrochloric acid, an excess of the latter being avoided, as it would disturb the formation of the green pigment. This will be brighter and lighter in shade in proportion as more chromium oxide has been combined with the phosphoric acid. It is therefore preferable to use, at the outset, a larger quantity of the calcium phosphate solution than is really needed to form the green. Hence the resulting product seems to have no constant composition, but rather to be a variable mixture of chromium phosphate and chromium hydroxide. Instead of cane sugar, the much cheaper glucose, and probably certain other cheap reducing agents, may be used.

Schnitzer's green is prepared in a similar manner. 72 parts of sodium phosphate and 12 parts of tartaric acid are treated with 30 parts of potassium bichromate. A green colour is obtained, which differs only a little from Plessy's green, but is far more expensive to produce.

Arnaudon's Green.—According to the inventor's instructions, this green is obtained by heating a mixture of 128 parts of neutral ammonium phosphate and 149 parts of potassium bichromate to about 200° C. The product obtained by careful working is said to compete with emerald green in brightness and shade, and in addition to possess the valuable qualities of chromium oxide. However, even if this should prove correct the high cost of producing this colour would greatly retard its general technical application; and this is actually the case at present. Therefore Arnaudon's green remains of merely scientific interest. On a small scale it can be made as follows:

The finely pulverised salts are intimately mixed in the above proportions by weight, and the mixture is heated in a basin to 170° to 180° C. To obtain a thoroughly intimate mixture of the materials, according to the instructions of the inventor, each salt is dissolved by itself in a little hot water, the solutions being then united, and the resulting liquid evaporated until a pasty consistence is attained. The mass, which sets on cooling, is ground to a coarse powder and heated in this state, as mentioned above. As soon as the temperature has risen to 180° C. the mass becomes soft again, intumesces suddenly, and passes over to the green combination, with liberation of steam and gaseous ammonia. The green increases in brightness when heated further up to 200° C. This temperature must be maintained for about half an hour, but if it be exceeded the green shade disappears again by gradually turning brown. The melt obtained at 200° C. must be washed with hot water, as explained in the manufacture of Guignet's green, the contained salts being thereby extracted and Arnaudon's green left behind in a very finely divided state.

The resulting green colour has in general the same properties as Guignet's green. Arnaudon's green resists the influence of acids and alkalies, is very fast to light, and is of a bright pure green shade, which it retains under artificial illumination. If calcined after drying, Arnaudon's green parts with water of hydration and changes its shade, being apparently transformed into the duller chromium oxide.

Dingler's green is a mixture of chromium and calcium phosphates. It is not so bright as Arnaudon's green.

Casali's green is obtained by heating 1 part of potassium bichromate with 3 parts of gypsum, and boiling the melt with very dilute hydrochloric acid. It is therefore pure chromium oxide, and possesses the same properties and characteristic shade.

The calcined chromium oxide will resist even boiling sulphuric acid, and therefore can be easily freed from all admixtures soluble in acids. When it is fused with soda and saltpetre on platinum foil or is boiled with potassium permanganate the corresponding alkali chromate is formed, soluble in water, and of a light yellow shade. Acidified with acetic acid, the solution turns yellowish red, and gives with lead a yellow, with mercury a red, and with silver a reddish brown precipitate. When the solution, however, is treated with ammonium sulphide or concentrated with hydrochloric acid a green shade is obtained. The borax bead also is coloured green in presence of chrome.

It was owing to the highly divergent colours of the compounds of this element that it first received the name "chromium," from the Greek χρῶμα (colour).

c. Green Cobalt Colours

Of this group of colours only two representatives are known: cobalt-zinc oxide, or *Rinmann's green*, and the alumina-chrome cobalt oxide, or *turquoise green*. The former possesses merely a theoretical interest, since it has never been put on the market. The latter is preferably used for glaze fluxes in porcelain and glass painting. Although the description of these colours hardly comes within the scope of this book, it will nevertheless be briefly noticed, turquoise green being used in isolated cases for painting in oils.

Rinmann's green was discovered in the last quarter of the eighteenth century by the Swede Rinmann, and was produced by heating a mixture of zinc oxide and cobaltous oxide, but was unable to find any practical application, on account of its high cost of production. Despite the successful manufacture of zinc oxide on a large scale and the greatly reduced cost of cobaltous oxide, Rinmann's green still failed to secure popularity, being neither specially bright nor of good covering power. The other properties—viz., perfect insensitiveness to all outside influences—are also possessed by the relatively much cheaper Guignet's green in the same, if not in a higher degree.

Rinmann's green, sometimes also called zinc green, can be prepared in different ways. The resulting colours seem to differ in composition and appearance according to the recipe followed, the shade increasing in lightness with the amount of zinc oxide present in the compound. According to one recipe, the dried precipitate, obtained by treating 16 parts of zinc sulphate and 7 parts of cobalt sulphate with potassium or sodium carbonate, must be heated to a very high temperature until no further increase in the intensity of the resulting green colour can be detected. Another method prescribes dissolving 1 part of cobalt oxide in the equivalent quantity of hydrochloric acid, the solution being treated with 10 parts of aluminium sulphate. The liquor is thickened with 50 to 100 parts of zinc oxide, dried, and finally very strongly calcined. As may be seen, these two recipes deviate considerably, so that their products may be assumed to consist of entirely different bodies.

An addition of phosphoric acid or arsenic acid is said to increase the brightness of Rinmann's green (according to *Louyet*). More recently, according to *Herter*, this green has also been obtained as a by-product in the metallurgical treatment of nickel ores. Rinmann's green can also be obtained in a particularly bright shade by calcining 100 parts of zinc sulphate and 2·5 parts of cobaltous nitrate.

Turquoise green, which has a highly blue tinge, cannot compete with the bright appearance of the cheaper Guignet's green. The brightest shade is obtained by heating to redness a dry mixture of 60 parts of soft, pulverised aluminium hydroxide, 30 parts of chromium hydroxide, and 30 parts of cobaltous carbonate. According to another recipe, a very bright turquoise green can be obtained by precipitating the mixed solutions of aluminium sulphate, of chromic sulphate, and cobaltous sulphate with a solution of soda. The thoroughly washed precipitate is then dried and heated to redness for some time.

Turquoise green is said to owe even its present limited application in porcelain painting entirely to the circumstance that the shade of the resulting glazes cannot be obtained by the use of any other materials or by mixing blue and yellow. The same property also influences its application in painting.

d. Ultramarine Green

The manufacture of ultramarine green has already been thoroughly described when dealing with that of ultramarine blue, so that we have now only to consider the details of the further treatment necessary to furnish a commercial article. Ultramarine green has only a very small covering power, and is therefore limited in its application as an oil colour. It is, however, valued as a transparent artist's colour, producing very fine effects; and it also does good service in litho and letterpress printing. Its chief technical application is, however, as a lime-wash, in which medium it gives a bluish green shade, very agreeable to the eye on account of its warm tone. Being fairly fast to light and air, ultramarine green is preferably employed for outdoor work, fronts, &c., either alone or mixed with other colours. In the last few years it has, however, been displaced by the so-called lime greens (made from coal tar dyes), which are not only cheaper and cover better, but are also nearly as fast to light and air, besides being brighter in shade.

The yellowish shades of ultramarine green are preferred. The bluish shades can be obtained easily, and above all cheaply, by suitable additions of ultramarine blue. Unfortunately, however, the finely pulverised yellowish ultramarine green, besides having the lowest covering power of all ultramarine brands, is more insignificant in appearance as the yellow tinge increases. As already seen in the manufacture of ultramarine, the faculty of giving yellowish ultramarine green belongs especially to the Glauber salt mixtures, which are the most important in the production of the commercial brands. The lighter shades of the more bluish soda greens are also often met with in the trade.

To obtain handsome yellowish green commercial ultramarines by calcining the Glauber salt mixture it is necessary to accelerate the process by forcing the rise in temperature, and taking care that none of the reducing agent is left unconsumed in the finished product. Should such be the case, the batch will generally be useless, for although it turns green at once in the air on being taken out of the furnace, the colour is irregular. These defective batches, however, can be used for making blue, the defect in question then becoming unimportant. A recurrence of the evil can be easily remedied at the next batch for green by decreasing the amount of the reducing agent, or, better still, by correspondingly longer raking. The green should then be uniformly soft, and showing as little blue as possible on the surface, a result obtainable by the employment of well-fitting lids and a reducing flame. Should the blue colour nevertheless be formed, the product must be carefully sorted, the blue portions being added to a batch for making blue, whilst the green portions can be re-sorted according to requirements. The differently shaded green sorts obtained in this manner are then ground separately in the dry state, washing now being regarded as unnecessary. The more or less fine products obtained in this manner are mixed for producing certain market brands (only two or three being usually made), according to proportions ascertained by trials on a small scale.

The foregoing remarks also apply to soda greens, which, however, will seldom stand such a strong grinding as the harder Glauber salt greens, owing to their much softer nature. For this reason the crushing is performed in the formerly described rolling barrels (*see* page 185), less, however, to obtain a finer powder than to ensure a more intimate mixture of the different shades of colour frequently present. The soda greens, as already mentioned, are of a more bluish shade than the Glauber salt greens, and therefore apparently more intense than the latter. This property is, however, only exhibited in the pure colours, for when mixed with white materials (as is customary for outdoor use) they have considerably less body than the Glauber salt greens.

The chemical character of the ultramarine greens is exactly the same as that of the different brands of ultramarine blue.

c. **Chrome Green** (*Green Vermilion, Chromgrün, Vert de Chrome*)

The so-called chrome greens are manufactured and used in larger quantities than any other green mineral colours. They are exclusively obtained by mixing chromes of definite shades with Prussian blue, finely ground barytes, which is taken up in almost unlimited quantities by the pure mixture, being added as a third ingredient, to obtain cheaper brands. The chrome greens are very strong in covering and colouring power, owing to the possession of the same qualities by the chromes and Prussian blue used in their preparation. This advantage is, of course, the chief reason for their extensive practical application, the more so because the capacity of the mixtures to stand large additions of barytes without unduly lightening the shade enables useful chrome greens to be produced at any required price. Chrome greens are not so fast to light as the zinc greens, but are nevertheless very largely used for outdoor painting, especially in oil, for which purpose their good covering power and low price may be the decisive factor. But whereas the zinc greens are specially used for oil paints, the chrome greens are also suitable as paper-stainer's colours, for litho printing, &c. In the manufacture of wall-papers they are known as *printing greens,* while in litho and letterpress work they are used under the name of *satin green* (Milori green).

On account of their great covering power, the chrome greens are specially suitable for mixing with other colours, provided the latter do not contain ingredients likely to act injuriously on their chemical properties. In consequence of the known sensitiveness of lead chromate and Prussian blue to even the weakest alkalies, the use of chrome green (even in oil) is precluded where such influences may be feared. The same applies to paintings exposed to even weak acids; for although the Prussian blue is proof against acids, the lead chromate of the green is destroyed by acid in a short time, or at least transformed into the straw-coloured modification, which will impart at least a bluish-white shade to the greens. This alteration is, of course, the more noticeable the smaller the content of Prussian blue—*i.e.,* the lighter the shade of the green. For mixing the chrome greens with size for wall-paper printing, or distemper painting in general, perfectly neutral size must be used; and on no account may the mixing be performed in a hot state, since the lead chromate present readily turns orange at high temperatures, and produces an olive green shade. For the same reason chrome green paints are inadvisable for articles exposed to high temperatures.

A very important part in the production of chrome greens is played by the selection of a suitable chrome yellow for obtaining the brightest shade, and furnishing a product with the highest capacity for resisting various influences. In view of the great variety in the shades of lead chromate, and still more on account of their great and sometimes inexplicable liability to alteration, the choice of and adherence to a suitable chrome yellow in order to obtain the same shade in all cases is one of the most difficult problems of the colour manufacturer. For instance, whether the mixing with Prussian blue is performed by the wet or dry process, any alteration of lead chromate (sometimes from apparently trifling causes) immediately results in the green being distinctly altered, sometimes to a far greater extent than the yellow itself. The chief fault, so far as concerns the manufacture of the chrome greens, is due to the fact that the chrome yellows used darken more easily (very likely on account of the presence of Prussian blue) than otherwise, thus making the greens dirty in shade, and consequently useless. This darkening, or rather orange toning, of the chromes may also appear even when a perfect green is kept for a long time in barrels or chests, no matter whether in a dry or damp place.

The proper shade of Prussian blue also has a great influence on the shade of the resulting chrome green. Prussian blue brands of a greenish tinge are precluded on account of the low intensity of the greens produced by their aid. This applies still more to the decidedly reddish brands of Prussian blue, these giving, in most cases, dull and even olive shades. It is therefore best to take a Prussian blue intermediate between a greenish and reddish tinge; but this is far more difficult in practice than appears at the first glance, since, for use in oil paint, consumers require the chrome greens to exhibit special properties, namely, that they must show up much darker and brighter when mixed with oils or varnish than they do in the dry state. Hence even the brightest chrome greens are of no use for oil painting if they turn paler or even whiter when mixed with the oil or varnish. Such paints will soon turn pale or dirty in colour, or become streaky or brittle under various influences. This property of showing up darker or brighter in oil is said to depend chiefly on the Prussian blue used, though the chrome yellow employed also has a certain, though smaller, influence on the result. This point must therefore be borne in mind in selecting the most suitable Prussian blue for making chrome green. This will, however, not be the case unless the intensity of the blue is very considerable—*i e.*, if it has been completely oxidised, a condition fulfilled by the Ia. brands of Prussian blue alone. It is therefore quite wrong to use any but the purest kinds of Prussian blue for the manufacture of chrome greens.

Besides the above-mentioned facts, the method of working is also an important factor. In the first place, a selection has to be made, in mixing chromate of lead with Prussian blue, whether the wet or dry process shall be adopted. Both methods can lead to successful, but not always to the same, results, and therefore the selection will be influenced solely by considerations of simplicity and reliability in working. The production of chrome greens in the wet way is rendered more difficult by the greater possibility of the lead chromate undergoing alteration than when the materials are mixed in the dry state. It has, however, the important advantage of securing the most intimate mixture of yellow and blue. Consequently the wet method affords greater certainty of obtaining perfect chrome greens than the dry process, where everything depends on the excellence of the machinery. A dry process of the kind under consideration implies that the mixing of the materials, chrome yellow, barytes, and Prussian blue, is effected by very careful grinding in edge-runners or balance wheels, the materials in question remaining in the dry state during the whole operation. Comparing the two processes, it will be obvious that they embody different means for the application of the Prussian blue. Thus, whilst in the dry process the blue can be used in the lump state in which it comes on the market, in the wet method it must be first brought into a suitable form—*i.e.*, it must be ground dry or wet. Now, in view of the great hardness of pure Prussian blue, it could never be converted by dry grinding into such a finely divided form as is required for the wet process. Hence for the wet method soluble Prussian blue, or better still, for reasons which will be given later on, blue in the form of paste, will be used. The great difficulty in properly grinding dry Prussian blue would stamp the dry process as a very uncertain one, were it not that the presence of (generally very large) quantities of barytes in the chrome green mixture greatly facilitates the mechanical distribution of the blue. For the same reason chemically pure brands of chrome green—*i.e.*, such as consist only of pure chromes and Prussian blue—cannot be manufactured at all by the dry method, the mechanical reduction of the blue taking such a long time to complete that the mixture would get hot in the mill, and thus cause a very disagreeable alteration of the chrome yellow. This notorious defect of the dry process is associated with certain other disadvantages, the consequence being that its exclusive employment in practice is out of the question. In view of the unlimited variety of the commercial brands of chrome greens, makers will scarcely be in a position to supply all demands from stock, but will rather be compelled to make up the greater part of their orders to sample from the stock grades. On the other hand, in view of the different methods employed in the various works, it will rarely be possible to match the shade of wet process chrome greens with those obtained by the dry process; and the necessity therefore arises of employing both processes, either concurrently or in suitable combination. The latter plan answers almost all the demands of consumers in respect of good quality product, and is therefore mostly employed in practice.

According to this mixed system the chrome greens are produced in different shades and prices by the wet way and then mixed in the dried state, adding chrome yellow, Prussian blue, or barytes, if necessary, to obtain a given definite shade. The capacity of barytes for taking up a considerable quantity of liquid Prussian blue (viz., finely ground with water) can be utilised here to very great advantage, since it obviates the necessity of adding pure Prussian blue to the dry chrome green mixture, and saves the time otherwise consumed in that operation. For this purpose the barytes is stirred up with water and mixed in a vat (by stirring) with a certain quantity of Prussian blue paste. After being dried and ground, the resulting product forms a blue powder, "*blued barytes*," sometimes found in the trade as "*mineral blue*." In our case, however, it merely replaces pure Prussian blue in the chrome green mixture.

The addition of Prussian blue in such a finely divided form as the blued barytes greatly accelerates the distribution of this colour in the green mixture, and thus lessens the danger of the chrome yellow changing unfavourably in the mixture through protracted working. In this manner brighter greens are always obtained than is the case with pure Prussian blue, provided one does not go too far in the opposite direction, for if the addition of blued barytes is pushed beyond a certain limit it may very easily happen that the chrome green will exhibit very disagreeable properties when ground in varnish, despite its bright appearance. One of the commonest and at the same time most objectionable features is that after a short time either the yellow or the blue, in the mixture with oil, will work out on the surface of the painting and entirely change its appearance when dry. This purely mechanical separation of the components is due to the difference of specific gravity, and is more certain to ensue in proportion as the amount of blued barytes in mixtures is raised and the care bestowed on the mixing is relaxed. It is therefore very important, when shading the wet-process chrome greens by means of blued barytes and chrome yellow, to see that the specific gravity of the adjunct approximates closely to that of the blued barytes—*i.e.*, to dilute the chrome yellow with barytes instead of using it in a pure state. For the same reason wet-process chrome greens low in barytes—viz., richer in chrome yellow and light in shade—must not be darkened by an addition of blued barytes, since in such event the difference in the specific gravity of the components would make itself felt in a very disagreeable manner on using these greens as oil paints.

In the manufacture of chrome greens by the wet process it is most important to use a possibly pale and bright chrome yellow as a basis. Of course the chrome yellow used must be fast to the Prussian blue in all stages of the manufacturing process. As already mentioned on several occasions, the chief risk of failure in the process is due to the tendency of the lead chromates to darken afterwards, and turn the greens an olive shade. This fatal alteration occurs very often even during the manufacturing process, shortly after the addition of the Prussian blue paste or during the filtering stage, and still more frequently in the drying-room. The causes may differ considerably, *e.g.*, defective manufacture of the chromes, insufficient purity of the Prussian blue, or faulty arrangement of the drying-room.

As already explained in detail in the section on chromes, the chrome yellows, regarded in accordance with their molecular composition as more or less allied to the basic lead chromates, have the strongest tendency to darken considerably during the different operations through which they have to pass before drying. Hence it is essential in manufacturing chrome yellow for the purpose now in view that this basic character should be avoided. Now this latter will always appear when basic lead acetate or potassium monochromate has been taken as a raw material, or if the precipitation has been effected hot. It therefore follows that in producing a suitable chrome yellow for making green, neutral lead acetate and potassium bichromate can alone be used, and that the chemical reaction must proceed at a low temperature only. The most reliable basis for chrome greens would therefore be the so-called lead sulpho-chromates already fully described on page 137. These chromes as a matter of fact give the brightest chrome greens, and are now largely used in making the popular chrome green resembling zinc green. On the other hand, they cannot be used for very dark green shades, since even the medium green shades have the defect of exhibiting a whitish appearance when used as oil paints, owing to their content of lead sulphate. To obtain suitable dark shades, especially such as will show up dark in oil, the chrome greens must have as a basis a chrome yellow considerably more reddish in tone than is possible with lead sulpho-chromates on account of their chemical composition.

With regard to the chrome yellows obtained from white lead, some of the lighter shades of these are suitable for the manufacture of nearly all shades of chrome greens; but it is not yet known whether such lead chromates are really used in practice for this purpose. On the other hand, the chromes made from lead nitrate (no matter whether crystallised or obtained by dissolving white lead in nitric acid) are useless, the resulting chrome greens having a poor appearance in the dry state, whilst in oil they are very pale, sometimes even of a whitish cast. They are apparently not very fast to air, for, according to the observations of trustworthy technical men, they soon turn (even in the dry state) into the objectionable olive shades, and then retain the cloudy-whitish tinge when mixed with oil.

Consequently there is only a single chrome yellow which will give bright, light, and also very dark, full shades of chrome greens, namely, that obtained by precipitating neutral lead acetate with potassium bichromate. Its production, however, will be attended with some difficulty, inasmuch as the method will have to be adapted to the circumstances existing at the works, and therefore a certain amount of insuccess will be inevitable at first. Nevertheless, when successful results have once been obtained, and the same lines are strictly followed thereafter, this method of manufacture, on the basis of personal experience, will always prove better than any other. The following instructions for making a suitable chrome yellow must therefore be regarded solely as a general indication of the methods to pursue.

The chrome yellow obtained by the simple precipitation of a solution of sugar of lead with potassium bichromate has the defect of darkening afterwards to a considerable extent even during the washing process, and care must therefore be taken to obtain the lightest possible shade from the beginning, in order to obtain a yellow which, after washing at least twice, and after the subsequent addition of Prussian blue, will stand the further darkening occurring during the operations of filtering, pressing, and drying without impairing the brightness of the resulting dried green. In order to reduce this inevitable darkening to an absolute minimum, it will be necessary to perform the requisite operations as quickly as possible, and also strictly to adhere to the quantities of materials shown by experience to be correct, so as not to risk the delays caused by any variation therefrom, since any such delay will endanger the success of the whole process. In manufacturing chrome greens, it is primarily essential, more so than with any other colour, that the labour and time should be carefully apportioned, in order that a satisfactory result may be obtained. The careful avoidance of any loss of time ensures advantages operating favourably on the result. The most important of these is secured by beginning the work in the morning, and accelerating matters so far during the day that the colour will be in the drying-room by the evening. Hereby the colour, which cannot stand a high temperature, even at the beginning, will be exposed to a gradually decreasing temperature during the night time, since the heating of the drying-rooms is not usually kept up at night; and this lowering of the temperature will greatly contribute to a satisfactory result. For this reason it is highly advisable to prepare the two solutions of sugar of lead and potassium bichromate a day in advance, so that the manufacture of the yellow can be begun early the following morning. For this purpose a large precipitation tank (*see* Fig. 1) must be used, to save time in washing the lead chromate. Two smaller vats (of equal dimensions) are also required for preparing the solutions; and these are mounted close to the precipitating tank, so that the liquids can be transferred from one to the other with ease. To avoid any delay, which is also dangerous even at this stage, it is highly advisable to arrange the tanks as represented in Fig. 6.

In one of the small tanks pure crystallised sugar of lead is dissolved in a minimum of hot water, and the solution is afterwards diluted with cold water until the temperature has fallen to 18-20° C. In the same manner a cold and very dilute solution of potassium bichromate is prepared in the second small tank. Both solutions are allowed to stand for the deposition of any impurities present. In the meanwhile the prescribed quantity of barytes is stirred up with water and strained through a fine sieve into the precipitation tank. This must next be filled about half full of cold water stirred up well, and left for the barytes to settle down. It must be noted that some kinds of barytes cannot be used for the manufacture of chrome greens by the wet method, since the presence of any large quantity of gypsum or calcium carbonate may spoil the whole process. Hence none but perfectly pure barytes can be used, or in case such is not available, the contained impurities must be removed entirely by dissolving them out with hydrochloric acid. The remaining mass is then washed several times with cold water, whereupon it is ready for use. In view of the necessities of the case, all samples of barytes intended for use in the manufacture of chrome greens must first be tested for the impurities in question.

The water above the barytes in the precipitation tank having been drawn off, the clear solution of sugar of lead is run in and the tank filled about three-quarters full of cold water. The bichromate solution is then slowly added in a thin stream with continued stirring, which is continued for at least half an hour without any interruption after all the bichromate is in, the precipitation tank having been completely filled with cold water. In this manner 15-16 parts of potassium bichromate and 48-50 parts of crystallised sugar of lead will furnish a very pale chrome yellow, containing the excess of sugar of lead absolutely necessary to prevent any formation of basic lead chromate. The yellow having settled down very quickly, on account of the barytes, the top liquid is drawn off, and a further solution of 1-1·5 parts of sugar of lead is added. After a couple of washings, with thorough stirring, the chrome yellow will be ready for taking up the Prussian blue. For this purpose the so-called "water-soluble" blue would be useful, were it not that this article is always expensive, whilst the makers' statement that it is free from acid is not always reliable. On this account it is too uncertain a product to be recommended for making chrome greens. It will be far better for the colour maker to prepare his own Prussian blue for this purpose, since he will then be able to rely on having an absolutely pure product free from acid. So far as shade is concerned, the most suitable of all brands of Prussian blue is that obtained by oxidation with sulphuric and nitric acid. It may be used either in a state of suspension in water or as a thin pap after having been filtered, but not pressed. If it cannot be made on the premises, it must be specially ordered from the blue manufactories as blue for chrome green, and can then be obtained as a paste of any desired consistence. The amount of Prussian blue (calculated on the basis of the dry matter) necessary to obtain the desired shade of green is made up to a thin pap with water and poured on to the chrome yellow in the tank through a sieve, and stirred continually to ensure uniform mixing. This done, the finished green is transferred to the filter, and when sufficiently drained is pressed at once as strongly as possible.

The method adopted for drying the chrome greens after leaving the press has a very important effect on the result. Quick drying is generally advisable, since the formation of basic lead chromate takes place rather quickly, even in the case of perfectly neutral lead chromate, when the product is left in a damp state any longer than absolutely necessary, whilst the presence of Prussian blue seems to accelerate its formation. It is absolutely wrong, however, to dry at a very high temperature in order to quicken the process, such temperatures having to be guarded against for reasons already mentioned. The finely-crumbled chrome green will dry quickly at a relatively low temperature (40° C.) if the atmosphere in the drying-room be kept as dry as possible by good ventilation to carry off the vapour liberated in the drying process. On the other hand, the supply of heat should also be regular, so as to prevent the temperature fluctuating, at one time rising above 40° C. and afterwards falling below it. The drying-room should be as lofty and airy as possible, and fitted with large drying-racks. If possible, steam heating should be avoided, hot air giving decidedly better results both with lead chromates and chrome greens. At any rate, great care should be taken that all the joints of the steam pipes and radiators are always steam-tight and will not admit steam into the room through leakages. In an efficient drying-room the strongly-pressed chrome green, crushed as small as possible, should dry in about twelve to eighteen hours, according to the season. No other colours should be dried in the same room with the chrome greens, since their presence will naturally retard the drying process in a manner disadvantageous to the green pigments.

It being, on the one hand, impossible to keep all the extremely numerous shades of commercial chrome green in stock, and, on the other, very difficult sometimes to match a required shade immediately, without any preliminary trials (on account of the alterability of the lead chromate), it is advisable to make a certain number of stock grades: say, a light, medium, and dark shade, for instance, in three to four different qualities (by adjusting the quantity of barytes). It is also advisable to keep these standard grades in a dried but not pulverised state. It will then be possible, by mixing these stock grades in certain proportions (determined by trial with small quantities) in the edge-runner mill, to match any desired shade and price quickly and accurately, blued barytes and chrome yellow being added if necessary. Chrome greens that have turned olive in the wet process can generally be worked up again in this way. The chrome green mixtures corresponding to the standard grades must be sifted after leaving the mill in a ball mill fitted with a continuous sifting device, or in a bolting mill, or ground direct in beater mills to a fine powder. The grinding of chrome greens, especially the lighter shades, between mill-stones is always risky, owing to the danger of the shade undergoing alteration if the stones get heated through lack of care in supervision.

The difficulty of producing a good bright chrome green by the wet method has caused a large number of recipes to be brought out for avoiding the rapid darkening of the chrome yellow, though in most cases the object is thwarted by the protracted and complicated methods of working proposed. It is therefore better to use the simplest possible process, as being less likely to cause loss of time with its attendant evils. In all cases, however, the process will require careful attention, so as to prevent untoward incidents, or at least to minimise their detrimental effect.

With regard to *silk greens*, these are generally made on the same principle as the chrome greens, except that blanc fixe is used instead of barytes. Commercial blanc fixe, however, is unsuitable for this purpose, since, even when the carrier has been brought into the state of distribution, the dried green (which is always made up into cones) exhibits on the surface of the fracture white specks of uncoloured blanc fixe thus of course lessening the value of the product. To avoid this defect, it is better to make the blanc fixe on the premises, and thus obtain the finest possible state of division. For this purpose a solution of barium chloride, diluted to about 20° B., must be precipitated with dilute sulphuric acid at 35° C. The barium sulphate precipitate is then washed free from acid with pure cold water, and the further treatment applied as mentioned for chrome green.

In the production of silk greens the danger of the darkening of the contained chrome yellow is far less imminent than with the chrome greens. Therefore, before being shaped into cones the green paste can be kept, without any special care, over night or still longer, especially if left in the press, and no risk of any considerable alteration need be feared.

f. Zinc Green (*Zinkgrün, Vert de Zinc*)

The so-called zinc greens share the popularity of chrome greens for outdoor use as oil paints, on account of their brightness combined with cheapness. They are colour mixtures of zinc chrome, barytes, and Prussian blue, and are made on similar lines to the chrome greens, except that the character of the zinc chromate replacing lead chromate in the mixture requires a somewhat longer mechanical treatment of the mixture. By the aid of zinc chrome* and Prussian blue it is possible to obtain a very long scale of green shades from the lightest parrot green to the deepest blue-green. All these mixtures have a quite different tone to the chrome greens. The latter are more inclined to olive green, and darken considerably in oil on account of the lemon shade of the lead chromate used; whereas the pure green shade of zinc green (like emerald green) remains unchanged, as the zinc chrome is permanent. The covering power of zinc green, however, is far less than that of chrome green.

The fastness of zinc green to light is good, and (as has been proved by extensive trials) considerably greater than that of chrome green of equal intensity. This striking property must be due to the zinc chrome, for since the same pigment, Prussian blue, is used in both cases, and there is no question of chemical combination in the merely mechanical process of mixing with the zinc or lead chromate, the decisive fact must necessarily be the greater fastness of the zinc yellow compared with lead chromate. This remarkable difference of the fastness to light can be tested by spreading samples of both pigments in the form of powder, and with the same content of Prussian blue, side by side, on paper and exposing them to the light for a short time. The chrome green very soon turns a yellowish shade, whereas the zinc green prepared with the same blue shows scarcely any change.

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* If the proportion of sulphuric acid and potassium bichromate are suitably changed two brands of zinc chrome for greens can be produced, one for bluish green, the other for rather yellowish shades. [TRANSLATOR.]

The difference is still more evident when a light zinc green and a dark chrome green, containing more Prussian blue, are mixed with oil and exposed to the light. No satisfactory explanation has yet been given of this difference.

On the other hand, zinc green, like chrome green, is not fast to lime.

A defect observed in zinc green as paints, still more frequently than with chrome greens, is the so-called "blueing" or "running," the paint becoming streaky and spotty, even on small surfaces.

The "blueing" is due to the Prussian blue in the zinc chromes making its way to the surface of the paint, imparting a checkered appearance to the surface of the coating, which is very seldom perfectly level. This appearance always occurs when the specific gravity of the zinc green is too heavy, on account of faulty manufacture, so that the lighter and very finely divided Prussian blue in the paint separates from the mixture.

Zinc green oil paint dries very hard, if suitably primed; it preserves wood very well, and protects iron successfully against rust.

The manufacture of zinc green is simpler than that of chrome green, on account of the greater fastness of zinc yellow. There are in this case also two ways of obtaining bright products. Either the zinc chrome whilst still in the tank (*see* page 128) can be directly coloured with the Prussian blue, as described already for the chrome greens (*see* page 248), or the materials, *zinc chrome, Prussian* blue, and *barytes,* are mixed in the dry state in an edge-runner mill. Both methods give bright shades of zinc green, and the only difference is the longer time taken by the first process than by the dry grinding of the materials.

To manufacture by the first method, the pasty zinc chrome must be diluted, after washing, with the necessary quantity of barytes (determined by the desired price of the green) and a measured quantity of Prussian blue stirred up with water to a thin pap, the whole being well mixed until no more uncoloured barytes or zinc chrome can be found in the mixture. It is then filtered, the pasty colour in the filter being thoroughly worked through from time to time. After the mass has drained to at least the consistence of a stiff paste, it is further mixed, either in a cone mill (Fig. 8), or, better still, a wet mill (Fig. 9), by which time nothing but the pure green shade will appear in the mixture. The colour is then pressed, cut in pieces, and dried at about 50° C. In this manner eight to ten different brands of zinc green, lighter and darker, and containing more or less of barytes, can be produced at prices that can be determined exactly. By mixing these various brands together in the dry state and adding barytes, zinc chrome, or Prussian blue, if necessary, in the edge-runner mill, it is possible to obtain a very long scale of zinc green shades corresponding to all requirements both in quality and price. This process, as already mentioned, gives very handsome greens, but takes up much time and room. It has also the defect that errors may arise in stirring the raw materials, and result in considerable loss. Hence the second method is preferable, since in this case only three raw materials have to be considered--viz., zinc chrome, barytes, and Prussian blue—so that any considerable error in calculation is precluded. Certainly an efficient and fairly heavy edge-runner mill is a prime necessity for this process.

The mixing of the dry materials to obtain a special classification of products must be effected on systematic lines. The first point is to obtain a certain number of chemically pure grades of zinc green. These are prepared by grinding zinc chrome and Prussian blue together, the gradation in shade being obtained by taking a stated quantity of zinc chrome and using progressively increasing weights of Prussian blue. For instance, the very light are graded by increasing the Prussian blue by half a unit (of weight) in each case, the increase for medium shades being 1 unit, and for the dark shades 2½ to 5 units. The next series will then be manufactured by a further addition of barytes, to the extent, for instance, of 10 per cent. of the weight of zinc chrome; the third 25 per cent., the fourth 50, 60, or 75 per cent.; the fifth 125 per cent., &c. In this manner a sufficiently varied range of grades will be obtained to enable almost any other makers' brands to be matched, both in shade and price. The mixing of the raw materials in the edge-runner mill must be continued until a perfectly uniform shade has been obtained. This can be tested by taking small samples of the mixture from time to time and spreading them out flat with a horn spatula on a small piece of white paper. If the colour still contains particles of Prussian blue, visible to the unaided eye, the grinding cannot yet be considered as finished, and must be continued until such particles have entirely disappeared. When, however, a second grinding on a balance or beater mill is contemplated—as is mostly the case—the mixing on the edge-runner mill need not be carried so far, the other mills giving a thorough finish to the grinding. If balance-mills are used the stones must not be allowed to get too hot, or the green will become hot and the colour impaired. For this reason the beater-mills are often preferred to mill-stones for this purpose.

The sifting of zinc green is attended with certain difficulties, especially with the better grades, *i.e.*, those low in barytes, the meshes of the sieve soon getting choked, so that finally the work has to be stopped altogether. Hence a thorough grinding is an essential preliminary to obtaining a perfect zinc green.

Zinc greens have also, in many cases, to be made so as to match a given sample, but as the variety of shades is not nearly so large as with chrome greens, there is much less difficulty in obtaining the desired shade with a little practice.

Whilst in manufacturing zinc green by the wet method the same Prussian blue can be used as for chrome greens, a dark brand of Milori blue (Chinese blue) is preferable for dry mixing. This not only gives brighter shades, but can also be mixed much quicker with the other materials (barytes and zinc chrome), on account of its softer nature, than the more brittle dry Prussian blue. The use of Milori blue, which has about the same specific gravity as the zinc chrome, minimises the danger of "blueing out," provided a high-class zinc chrome has been used. Under certain circumstances "blued barytes" can also advantageously be employed for mixing (for the preparation of this mineral see Chrome Greens), but the resulting greens are more liable to "blue out" when mixed with oil than any other brands of zinc green.

g. Permanent Green

The manufacture of permanent green is performed exclusively by the dry method, in precisely the same way as zinc green so far as the mechanical treatment of the materials is concerned. The raw materials in this case are Guignet's green, zinc chrome, and barytes. The use of lead chromates instead of zinc chrome (entirely or only in part) is rare, such mixtures giving shades that are neither bright nor permanent. Pure permanent greens, or those containing only a very little barytes, are of a very bright shade, closely resembling emerald green, especially when mixed well in oil, but they are generally of only moderate covering power. The circumstance that Guignet's green loses its brightness under protracted grinding naturally affects its treatment in making permanent green, for though the bright shade of the latter in oil may not be changed very much by extensive grinding, the dry greens always lack brightness, a defect naturally increased by the addition of barytes. Hence any excessive grinding of the permanent greens is always a risky step, when they are desired to look bright in the dry state. Permanent greens are very seldom used as distemper colours, as they can be easily replaced by green aniline lakes, which are considerably brighter. Their application for other purposes, however—*e.g.*, printing on cotton, wall-papers, &c.—usually entails very fine grinding, which therefore cannot always be avoided.

Since neither the Guignet's green nor zinc chrome has good covering power, their pulverised mixtures (no matter in what proportions) always form very loose powders very liable to throw off dust and increase the difficulty of their further treatment. To obviate this defect the mixture in the edge-runner mill may be treated with any suitable binding medium - *e.g* , glycerin, mineral oil, &c.—which at the same time brightens the appearance of the colour. The addition of these media cannot be considered as an adulteration, since it really constitutes an improvement by preventing otherwise inevitable losses due to the formation of dust.

The proportions in which the materials used for permanent green can be mixed are more limited than for zinc green, as in this case specially light shades alone have to be considered; and moreover, the use of barytes is restricted on account of the moderate covering power of the Guignet's green and zinc chrome.

Hence only a few standard brands are generally kept stocked, and these are compounded mostly in three gradations—light, medium, and dark, two qualities of each. The following table may serve as a typical example :

	I. Grade (chemically pure).			II. Grade.		
	Light.	Medium.	Dark.	Light.	Medium.	Dark.
Guignet's green .	40	60	80	40	50	60
Zinc chrome . .	60	40	20	50	40	30
Barytes . . .	—	—	—	10	10	10

These proportions can, of course, be changed according to desire or taste, but it will soon be found in practice that no very wide range is feasible. To obtain pure green shades Guignet's green should be predominant in the mixture, on account of its inferior covering power, and therefore the variety of shade is limited.

h. Olive Green

Within the last few years olive greens have come so much into favour, not only for wall-paper designs, but also for distemper and oil paints for interior and outdoor use, that one may almost speak of a "mode colour" in this connection. The variety of olive shades is nearly unlimited, at least in a technical sense, since it embraces all greenish tones, starting from very pale yellowish green, and extending through red, brown, and blue greens to the deepest dark green, furnishing a colour scale of a magnitude not exceeded even by the lead chromates.

As a basis for the purer brands of olive greens a dark chrome yellow is always used, which, on account of its high covering power, can be mixed with other colours inferior in this respect, and still furnish useful products for various kinds of paints, even though it forms only a very small part of the mixture.

The purest olive green shades are obtained by mixing dark lead chromate with Prussian blue. In proportion as the basic character of the chrome yellow increases the resulting olive greens, with the same quantity of Prussian blue, become more reddish in tone, appearing fuller and less agreeable to the eye. Given a constant quantity and shade of chrome yellow in the mixture, the lighter shades of olive green are obtained by gradually diminishing the quantities of Prussian blue, the converse procedure giving the dark olive green shades. Even in this simple manner a very wide scale of tones is obtained, and this can be still further amplified by using lead chromate of a gradually increasing basic character. Moreover, when the limits possible with a maximum of Prussian blue have been attained, a new and still more extensively graduated group can be obtained by adding certain quantities of black. Additional modifications will result according to the brownish or bluish tone of the black itself, so that the number of olive green shades is practically unlimited, especially in view of the gradations imparted by the further addition of brown, red, and white of various shades to the original olive green mixtures. In this way the number of olive green shades can be increased to an extent that cannot be realised with any other group of colours.

To manufacture the olive green for outdoor and interior paints, the different kinds of black pigments, such as mineral black, Frankfurt black, ebony black, lamp black, &c., as well as the brown earth colours, raw and burnt umber, dark ochre, terra de Siena, come under consideration, whilst as a white diluent barytes is almost exclusively used. Of the blue colours Prussian blue is chiefly used, more rarely ultramarine blue. Naturally, too, the faulty chrome greens that have changed colour, and defective batches of zinc greens too, can be utilised for making various shades of olive green.

On account of their great variety the matching of olive green samples requires thorough knowledge of the effects obtainable by mixing together the above mentioned mineral and earth colours, and therefore the possession of an acute sense of colour and great skill. Otherwise it may easily happen that the exact matching of a given sample may take days or even weeks, unless a happy accident supervenes to shorten the task.

Manganese Green.—A certain number of manganese compounds are known as green pigments, but are very little used.

Cassel green (*Rosenstiehl green*) is produced by heating a mixture of manganese oxide or manganese nitrate with barium nitrate. A mixture of manganese carbonate, manganese peroxide, and barium peroxide is sometimes used as well. The heating of the mixture must not be pushed so far as to melt the mass.

Böttger treats manganese peroxide and potassium nitrate with fused alkali, manganese chlorate being obtained, a salt forming a green solution in water. This solution is precipitated by barium nitrate, whereby barium manganate is obtained as a violet mass. The washed and dried precipitate is then mixed with barium hydroxide and heated afterwards, the heated product assuming a pure green colour. It must then be washed with water and treated further.

Clermont uses manganese sulphide as a green colour. Pure manganous oxide, obtained by precipitating manganese sulphate with soda, followed by calcination, can also be used as a green colour.

RED MINERAL COLOURS

A certain number of red coloured inorganic compounds suitable as pigments have been known from the earliest times. At present, however, only three of these colours are practically used. These are *red lead*, *vermilion*, and *chrome red*. Whereas the first-named two pigments have been used in practice for many centuries—vermilion was known to the ancients—the manufacture of chrome red is of recent date, viz., since the discovery of chrome and the properties of its compounds. The other red mineral colours are now rarely found in commerce, and only in small quantities, so that they are of merely scientific interest. They will therefore be only briefly mentioned here.

Of the above red mineral colours, *red lead*, being cheaply produced, is very much used for paint, and is therefore manufactured on a large scale. Its extensive application, however, is less due to its bright shade than to its capacity for giving with varnish an extremely hard and tough coating, which greatly preserves iron and wood. The application of *vermilion* is less extensive. Vermilion, as a mercury compound, is very dear—the dearest mineral colour known—and therefore is not used for ordinary paints, its poisonous properties, moreover, precluding its more general employment. *Chrome red* has considerably declined in popularity during the last few years, owing to its relatively high cost of production and low covering power, especially in the darker shades, which are of a more crystalline character. It has also a low power of resisting external influences.

A still more potent cause for the decline of the red mineral colours is the development of the coal-tar colour industry, which has put on the market a large number of red organic colours that can be made up in a very simple manner as equivalent substitutes for chrome red and the dearer vermilion. These colours, which will be described later on with the aniline lakes, are not only made more cheaply and with greater certainty, but they are also generally brighter, fast to light and lime, and of a higher covering power, without possessing any properties detrimental to paints compounded with oil or varnish.

The red mineral colours may be divided into the following groups:

a. Red Lead Colours

Red Lead (*Minium*), an oxidation product of lead, has the formula Pb_3O_4 (or Pb_4O_5).

Chrome Red, basic lead chromate, has the formula $Pb_2(OH)_2CrO_4$.

b. Red Mercury Colours

Vermilion, mercury sulphide, HgS, a compound of mercury and sulphur.

Scarlet (*brilliant scarlet*), mercury iodide, HgI_2.

Mercury Chromate, Hg_2CrO_4.

c. Red Copper Colours

Copper Ferrocyanide, Cu_2FeCy_6.

d. Red Antimony Colours

Antimony Vermilion, antimony oxysulphide, $Sb_6S_6O_3$.

e. Red Cobalt Colours

Cobalt Pink (*Magnesia Pink*).

a. RED LEAD COLOURS

Red Lead (*Minium, Mennige*)

Red lead is known in the trade in two different brands, of deep orange to scarlet red shade. The lighter and at the same time finer brand is the so-called *orange lead* (Paris red, Goldsatinnober, &c.); the darker one (of a pronounced crystalline character) is known as *true red lead* (or crystallmennige). This latter brand is of less value than the orange red, and is always lower in price.

The manufacture of red lead was formerly confined to England. In the last five years, however, Germany also manufactures red lead on a very large scale. The most important centres of the industry there are Saxony and Bavaria, but especially Cologne.

Red lead is obtained by heating lead oxide PbO (massicot) in presence of air. According to its chemical composition, red lead is a higher stage of oxidation of metallic lead, the formula being Pb_3O_4. On account of its characteristic behaviour toward nitric acid, red lead must be regarded as a combination of lead peroxide with lead oxide. On treating red lead with that acid it is converted into lead nitrate, a deep brown insoluble lead peroxide remaining behind. After prolonged heating with an excess of nitric acid and an addition of alcohol, this residue is also converted into lead nitrate, the alcohol being reduced to ethyl aldehyde.

$$Pb_3O_4 = \underbrace{2PbO, PbO_2}_{\text{Lead oxide, lead peroxide.}}$$

$$2PbO, PbO_2 + \underbrace{4HNO_3}_{\text{Nitric acid}} = \underbrace{2Pb(NO_3)_2}_{\text{Lead nitrate}} + \underbrace{PbO_2}_{\text{Lead peroxide}} + 2H_2O.$$

$$PbO_2 + 2HNO_3 + \underbrace{CH_3, CH_2(OH)}_{\text{Alcohol}} = Pb(NO_3)_2 + \underbrace{CH_3, COH}_{\text{Aldehyde}} + 2H_2O.$$

The behaviour of the alcohol during this process can be utilised in testing for any insoluble adulterants in red lead, such, for instance, as barytes, brick-dust, &c.

In accordance with its (theoretically) simple process of formation, red lead is manufactured by two methods differing little from one another—in fact, the difference exists only in the production of lead oxide from different raw materials: metallic lead and basic lead carbonate (lead white), or latterly lead sulphate as well. The chemical reaction of the conversion of the lead oxide into red lead is absolutely the same in both cases, except that the different construction of the oxidising furnaces sometimes necessitates a modification of the mechanical treatment employed.

The manufacture of the red lead is therefore divided into two special stages:

(1) Preparing the lead oxide, and

(2) Converting this product into the next higher stage of oxidation, according to the formula Pb_3O_4 (or Pb_4O_5).

As already mentioned, there are two modifications of the red oxide of lead with the same chemical composition PbO, but of different shades, and sometimes of quite different behaviour too. The one modification, of a more reddish shade, is the already mentioned *litharge*; the other, of a more or less pale yellow shade, is known as *massicot*. Before the various chrome yellows were introduced, the latter had a considerable vogue as a material for paint, and was invariably obtained by heating white lead, which at a high temperature loses its water of hydration and carbonic acid, massicot being left as a soft, pale yellow powder.

$$\underbrace{2PbCO_3, Pb(OH)_2}_{\text{White lead}} = \underbrace{3PbO}_{\text{Massicot}} + \underbrace{2CO_2}_{\text{Carbonic acid}} + H_2O.$$

At present the production of massicot, technically called *dross* or *casing*, is effected by heating metallic lead in a reverberatory furnace, the cost being much less than the white lead process. In the fused state it forms a glass-like mass, the so-called *lead-glass*. *Litharge* is obtained as a by-product in the metallurgical treatment of silver, and must be considered as fused, crystalline lead oxide, requiring to be ground in order to furnish the commercial powder form.

This form of litharge is not suitable for the manufacture of red lead, since it cannot be further oxidised. The names litharge and massicot therefore indicate two quite different trade products, and the statement in old text-books, &c., that litharge forms the raw material for the manufacture of red lead, is contradictory.

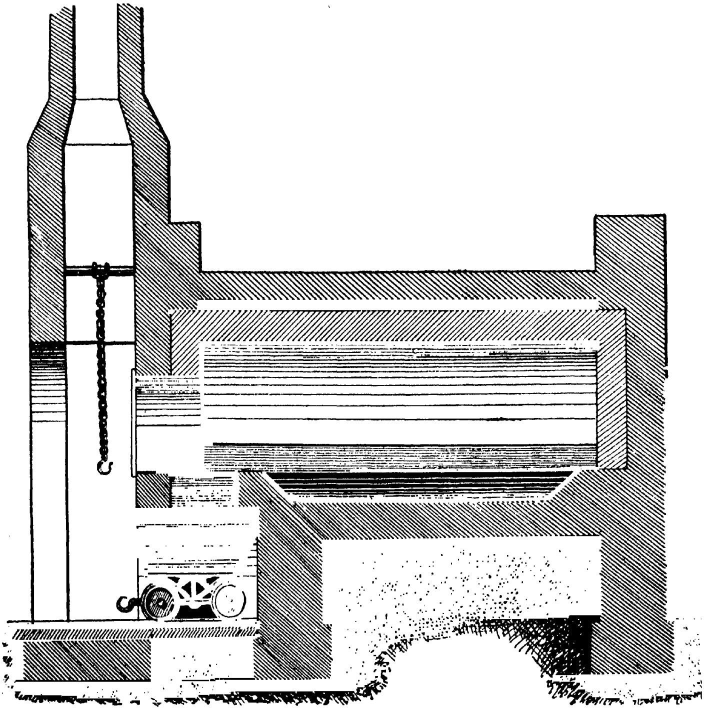
The manufacture of red lead is less difficult than is generally believed. With proper attention a favourable result may be expected in most cases if pure lead be always used and the first operation, the so-called "drossing," is carried out properly. The purer, softer, and finer the state of division of this product, the quicker and more certain will be the formation of a perfect red lead.

The oxidation of the metallic lead to "dross"—the so-called *drossing*—is performed in specially constructed reverberatory furnaces, the shape and dimensions of which depend on the size of this branch of the works. The chief object of the various kinds of these furnaces (nearly all of English origin) is, of course, to facilitate to the utmost the effect of the atmospheric oxygen on the molten lead, so as to shorten the process, work up the whole of the lead, and enable the work to be done with large charges of that metal. Owing to the obvious difficulty of combining these conditions in a single furnace, such a number of types have been proposed that it is by no means easy to ascertain which of them is really useful. A type of drossing furnace is represented in Figs. 73 and 74, which will explain the technical work of the "drossing" process, so as to enable the reader to form an opinion on the utility of other varieties of furnace.

In the largest works, too, at present, separate furnaces are used for the "drossing process" and the subsequent calcining process. It therefore seems evident that the endeavour to construct furnaces for serving both purposes has not been successful.

The "drossing" furnace is, as already mentioned, of the reverberatory type. Since it is intended to hold a large quantity of molten lead, which must be kept continually stirred, the furnace bed is trough-shaped and either elliptical or rectangular. The latter form seems to be more advantageous, since it is most used in practice. In the majority of cases the bed or hearth is covered with a strong arch, provided with a covering lagging of insulating material (ashes, sand, &c.) to prevent loss of heat, and topped by a level roof. The heat is generated in two fireplaces on either side of the bed, and in such a way that the flame passes over the molten lead in the furnace bed and laves all the surface of the vault. The fuel gases and the other gases and vapours liberated in the oxidising process pass off through a flue over the vault leading to the main chimney. The fireplaces may be provided with bars or be quite plain, and the arrangement in this respect, though it makes little difference to the heating effect obtained, has a considerable influence on the choice of fuel, the use of fire-bars enabling smaller coal to be burned. The fireplaces extend right along the side of the furnace, and are bounded by low walls on the side next the bed. The bed is generally about 12 in. deep in the middle, the sides being gently sloped outward all the way round. This arrangement is very important, and its purpose will be explained later. The front side of the furnace has three doors: the two side ones are for stoking the fires, while the centre door is for charging and emptying the furnace as well as for working the charge during the process. The air needed for oxidising the lead is supplied in a very simple way. The top part of the centre door, which is placed a little higher than the two side doors, is left open (or preferably covered with a damper). In the free space between the door and the furnace bed is a rectangular opening, through which the crude "dross" can be discharged into iron tanks underneath. To prevent any dissemination of dust, viz., any inconvenience to the work-people in this operation, the hollow space where collecting tanks are contained is closed by an iron door. The "dross" being specifically heavy, it is suitable, in view of the large quantities to be handled, to use wheeled tanks running on rails as described in Fig. 73.

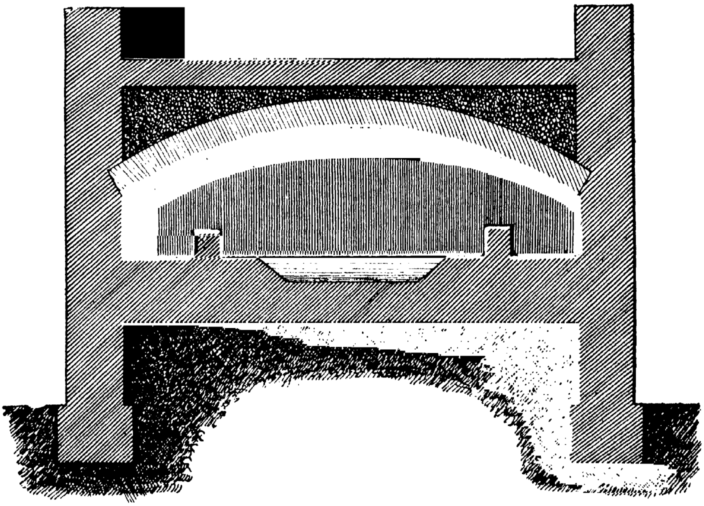
FIG. 73.



These arrangements are common to all "drossing" furnaces, and any modifications that may exist will refer merely to points of detail.

"Drossing" with such a furnace is a fairly simple process. The furnace being raised to a dull red heat, the charge of metal is inserted. The molten lead is prevented from flowing out of the furnace by a dam, formed of pieces of dross or "leavings" from previous batches, laid across the front of the bed. The molten lead becomes rapidly coated with a layer of oxide, the formation of which is hastened by raking the superficial layer of oxide to the front end of the furnace on to the bridge, the object being to always have a fresh surface of lead exposed to the oxidising action of the air passing through the furnace. At intervals pigs of lead are thrown into the furnace. This "drossing" process takes about 10–12 hours, at the end of which time the dam across the front of the furnace is broken down and the unoxidised lead allowed to run out, while the "dross" (the "casing") is taken out to be worked for the next stage. The furnace is then ready for a fresh charge. A dull red heat must not be exceeded in any case. The rakes for working the lead must of course be of iron and of a length corresponding to the dimensions of the furnace. The rakes being in most cases too heavy for one man to hold very long, they are generally suspended by a strong chain at the front side of the furnace, generally hanging from a movable crane in the front end of the furnace, the whole forming a kind of lever and enabling the raking to be done without much trouble.

Fig. 74.

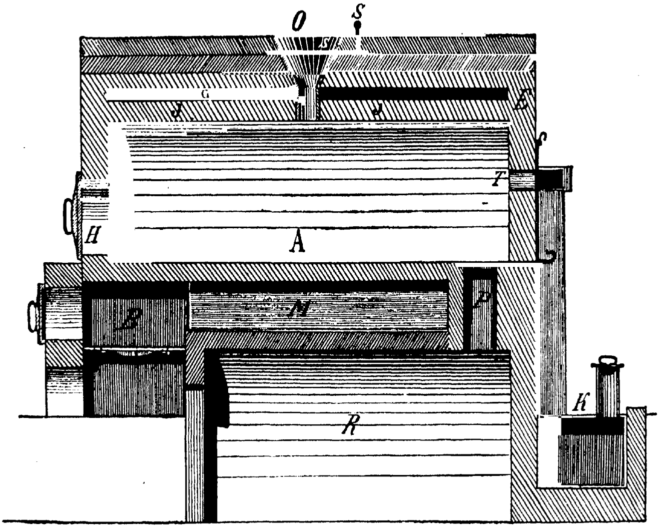


Generally about one sixth of the charge remains unoxidised for working with the next batch.

The "dross" forms a rather loose pale yellow to greenish yellow mass, and cannot be treated further in this state, but must first be made into a thin paste and ground, in order to separate the "dross" from the final traces of adherent lead and get it into the best condition for the calcining process, *i.e.*, into the finest possible state of division, since on this depends not only the brightness and shade of the resulting red lead, but also its covering power and other important properties.

The high specific gravity and the loose nature of the dross facilitate the combination of the washing and grinding processes. Wet mills (Fig. 9), fitted with hopper and feeding jig (like balance-mills), are used, and the whole set of mills discharge into a common collecting tank. The "dross" coming out of the furnace is washed with a stream of water to minimise the formation of dust in the working process, and is then ground immediately.

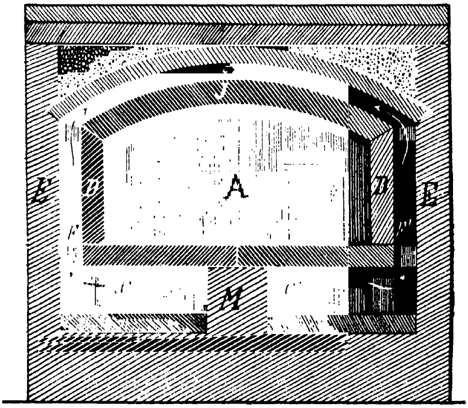
FIG. 75.



The wet mills are mounted, as described on p. 24, in rows of four. The collecting tank is fitted with a mechanical stirring apparatus driven from the mill shafting. From this tank the "dross" is transferred to a large wooden vat to settle down free from all residual lead. The arrangement of the whole plant enables the work to be carried on with a continual stream of water, thus simplifying and accelerating the task considerably.

The washing process is briefly as follows: The mills being charged with the "dross," the stones are set going, and a thin stream of water is admitted to each mill. The thin paste issuing from the mill runs down continually into a gutter wherein a considerable portion of the residual metallic lead will settle, together with the coarser particles of the "dross"; consequently, in order to prevent obstruction, a thin stream of water is run into the gutter from time to time, to flush the adherent particles of "dross" into the tank. The latter is shallow, to facilitate placing it in position under the mills and to accelerate the flow of the finely ground particles into the settling tank. The coarser particles of the "dross" and the metallic admixtures remain in the collector, whilst the finer and the finest particles run through an opening at the side into the settling tank. This latter, of course, must be placed at a still lower level. When it is filled up completely and no other is at disposal, the work must of course be interrupted until the "dross" has entirely settled down, which, however, generally takes only a very short time. The top liquor is syphoned off, and the operations are repeated until the whole stock of "dross" is worked.

FIG. 76.



The collected residues, coarse "dross" and granules of metallic lead, amounting to 10 to 25 per cent. of the weight of the "dross," are dried and oxidised over again.

The washed "dross" is afterwards filtered, dried, and in most manufactories is ground dry to a very fine powder in edge-runner mills.

In large works the washing process can, of course, be performed in various other ways, according to the local conditions, and, in fact, nearly all English red lead works have their own special systems.

Experience teaches that a bright red lead is unobtainable if the flame comes into direct contact with the product. Therefore in well-managed works a kind of muffle furnace is now used for the *calcining operation*. This plan, which was recommended by *Mercier*, is illustrated in Figs. 75 and 76.

The furnace consists principally of a roomy muffle, *A*, heated by two fireplaces, *B*, *B*. The bed of the muffle is made of large earthenware plates so as to be perfectly even. Below, and exactly in the middle of the hearth, is a strong wall, *M*, extending from front to back, supporting the hearth plates and dividing the space below into equal channels, *C*, *C*, forming a continuation of the fireplaces. The muffle is covered with a vault $4\frac{1}{2}$ to $5\frac{1}{2}$ ins. thick supported by strong side walls, *D*, *D*. *E* represents the outside wall. This furnace has the advantage of needing fewer repairs than older types. To accelerate the calcining process, the side walls and the vault of the furnace must be bathed by the heat, for which purpose flues are arranged between the side plates of the muffle and the outside walls, connected with the flues *C*, *C*, and leading the gases through the openings *F*, *F*, into the hollow space *G*, *G*, between the vault *J* of the muffle and the outside wall *E*. From here the gases pass away directly into the main chimney. As can be easily seen, the red lead muffle furnace is very similar in its interior arrangement to the ultramarine furnace or the retort furnace used for Guignet's green; only it is of much larger dimensions, and must therefore be more strongly built.

The red lead furnace is charged and emptied, through the opening *H*, or when the quicker handling of large quantities is in question by special arrangements for each operation, as shown in the figure. For greater convenience the opening *O* is arranged in the vault *J*, and is closed during the heating process by the small damper *SS*. In charging the muffle the "dross" is put in through the opening *O*, and as it falls on the hearth it is spread out to a depth of about an inch by means of an iron crook inserted through the opening *H*. The furnace is emptied by raking the charge out through the opening *P*, where it falls into a small truck in the chamber *R*. This truck runs on rails, and conveys the red lead into the rooms where the further treatment is carried on. The opening *P* is closed by means of a cast iron plate.

The supply of atmospheric air, which also serves in this case as the oxidising agent, is admitted by the two small openings *T*, *T'*, to the rear of the muffle, in such a way that the draught always flows from the front to the back. For this purpose the doors of the openings *H*, *H*, are fitted with movable sliding shutters, a little lower down than the two projections *T*, *T'*. Round or rectangular openings, *N*, *N* (Fig. 77), are sometimes arranged on either side of the working door for the same purpose.

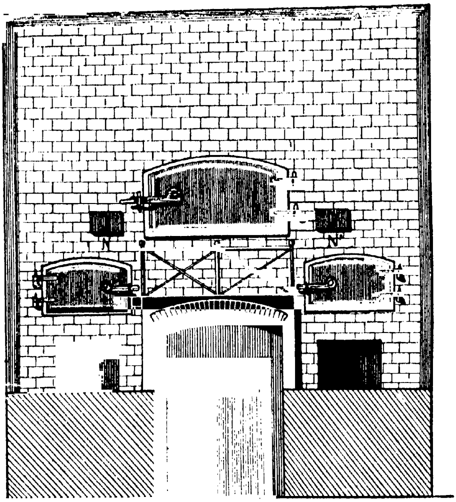
Under the powerful draught inevitable in the muffle certain quantities of the "dross" may be carried away past projections *T*, *T'*, and be lost. For collecting this dust the projections *T*, *T'*, communicate with an iron vessel *K*, let in the ground to collect the "dross" thus carried off through *T*, *T'*.

These red lead furnaces are most easily worked in the following way. The muffle having been brought to the proper temperature, *i.e.*, somewhat below a dull red heat, the charge of "dross" is admitted.

The mass is spread in a uniform layer all over the hearth of the muffle, special care being taken to prevent "balling" of the massicot—a condition that easily occurs in consequence of the sintering of the lead oxide when the temperature has risen too high. The resulting red lead would also be lumpy and require screening, the calcined product being also less bright and of lower value. Under careless management the "balling" of the red lead may proceed so far as to necessitate regrinding, which impairs the brightness to an even greater extent. The foregoing statements indicate that too much care cannot be taken in maintaining the right temperature.

When the charge is all in, the openings *H*, *H*, and the funnel-opening *O* are closed, and the necessary draught set up. Care has to be taken that too much draught is avoided, as this always produces a considerable loss of massicot. Once the necessary draught has been secured, there will then be no need to shift the dampers again, unless the temperature has risen too high and necessitates the sudden opening of all the dampers and plates. For this reason it is advisable to close the openings *H*, *H*, not with loose bricks, but by strong iron doors, since these can be opened and the furnace cooled more quickly in the event of an overheated muffle.

FIG. 77.



The chemical reaction of the muffle proceeds, according to experience, at certain definite temperatures, whereby an excess of air has no influence at all. A strong draught, therefore, will not affect the reaction, whilst it affords a means of keeping the muffle temperature at the proper limit.

On the other hand, an insufficient supply of air is always prejudicial, not only by retarding the whole oxidising process, but also from the danger it entails of overheating the muffle, and consequently of the aforesaid injurious "balling" of the charge.

The duration of the calcining process depends on the purity and the fineness of the "dross" used. Under favourable conditions of material and management the calcining process is independent of the dimensions of the muffle, and will generally be finished in twelve to fifteen hours, but may also take twenty to twenty-five hours. The duration of the calcining process, however, seems to have little influence on the brightness of the product, provided all the necessary conditions have been observed. The oxidation can be accelerated by employing hot air.

The oxidising process may be considered to be finished when samples taken from different parts of the furnace no longer show any increase in the brightness of the red lead. This being the case, the muffle can be emptied. If all these operations have been performed according to the prescriptions given above, and especially if a real first-class "dross" has been used, the resulting red lead will form, on cooling, a uniform powder with regard to fineness and shade. The product, however, must be resifted if any lumps are noticeable. The sifting will in this case be performed in such a way as to protect the red lead crystals, and therefore the machines used for this purpose must be selected carefully. According to experience, large ball-mills with continuous sifting devices are the best, since by reason of the density of the red lead they will sift it properly, even without using the balls, provided a fairly good calcination product is taken. The rotation of the machine soon breaks down the lumps by their own weight without injuring the crystals, a speed of at least 40 to 50 revs. per minute being necessary to secure this result.

The red lead, prepared from metallic lead as described, is sometimes, especially in Germany, called *crystal red lead,* and being cheaper, is more largely used than the brighter and finer orange lead. It is chiefly used as an oil paint for iron pipes, machinery, vessels, &c.: also for painting wood that is constantly exposed to moisture—*e.g.*, barrels, vats, tanks, &c. The property of red lead to form with linseed oil paints that dry very quickly and extremely hard explains its great advantages and extensive application. Another well-known use for red lead is as a packing for tightening joints, &c.

Orange lead is always manufactured by calcining powdered white lead. As already mentioned, white lead decomposes at higher temperature to lead oxide (dross), carbonic acid, and water, these latter escaping as vapour. The "dross" is then oxidised, as is done in the manufacture of red lead. Owing to the purer quality of the white lead the resulting dross is of perfect quality, and therefore needs no preparation before being worked up into orange lead. The manufacture of the orange lead is therefore performed in a single stage directly from the white lead, exactly as mentioned for (crystal) red lead, and in the same furnaces (Figs. 75, 76, and 77).

The furnace is, however, somewhat modified, the muffle *A* being connected directly with the chimney by an iron pipe provided with a device for regulating the draught. This enables the considerable quantities of carbonic acid and water vapour to escape during the decomposition of the white lead, without unduly cooling the furnace.

The shade of the white lead to manufacture orange lead seems to have but little influence on the brightness of the resulting product. Therefore the manufacturers prefer using white lead that is not quite pure enough in shade for use in paint. Whether the white lead has been manufactured on the Dutch, German, or French method is also immaterial. Neutral lead carbonate too, $PbCO_3$, furnishes a good product when heated with sodium nitrate at red heat (see p. 267).

The only other inorganic lead salt suitable for making red lead is lead sulphate, on account of its low price; but this consideration is outweighed by the more troublesome method of treatment involved, a fact which probably explains why this alternative material is now very little used. The process is briefly as follows: Commercial lead sulphate is sold in the form of a more or less stiff paste, and always contains a large quantity of impurities, viz., acetic acid, aluminium sulphate, aluminium hydroxide, sand, &c., from which it has to be freed before use. The acetic acid and aluminium sulphate are easily eliminated by washing with water; the mechanical impurities, sand, particles of wood, &c., can be removed by passing the thin pap of sulphate through a fine silk sieve. The admixed aluminium hydroxide, about 2 per cent. or more, cannot be easily eliminated, and generally remains in the mass, on account of the high cost of suitable treatment. The pure lead sulphate is then dried and ground to a fine powder.

The conversion of the lead sulphate into red lead is effected by the aid of sodium carbonate and sodium nitrate in such a way that sodium sulphate and lead carbonate are formed, the latter being oxidised by the sodium nitrate to red lead, Pb_3O_4, with escape of carbonic acid. The chemical reaction occurring at about dull red heat is expressed by the following equation:

$$\underbrace{6PbSO_4}_{\text{Lead sulphate}} + \underbrace{6Na_2CO_3}_{\text{Soda}} = \underbrace{6PbCO_3}_{\text{Lead carbonate}} + \underbrace{6Na_2SO_4}_{\text{Sodium sulphate.}}$$

$$\underbrace{6PbCO_3}_{\text{Lead carbonate}} + \underbrace{2NaNO_3}_{\text{Sodium nitrate}} = \underbrace{2Pb_3O_4}_{\text{Red lead}} + \underbrace{6CO_2}_{\text{Carbonic acid}} + \underbrace{2NaNO_2}_{\text{Sodium nitrite.}}$$

The proportions are 110 parts of dry lead sulphate, 39 calcined soda, 8·5 of sodium nitrate. Experience shows, however, an excess of the sodium nitrate gives a better product. The smelt consists of a mixture of red lead, sodium sulphate, and sodium nitrate, besides variable quantities of undecomposed nitrate. These three latter salts are removed by leaching with cold water, the red lead being afterwards filtered and dried. The red lead obtained by this method is a dark orange, soft, and very bright powder of good covering power. Unfortunately this method is profitable only when the resulting liquors can be treated for the recovery of their contents, which can seldom be done.

Chrome Red

The formation of chrome red, the most basic lead chromate, was briefly mentioned in discussing orange chrome. Referring to the chemical equations given on p. 144 to explain the composition of the basic lead chromates and their method of formation, the production of chrome red can be expressed by the following equation, the quantity of lead oxide in the basic lead acetate being taken as N = 1:

$$\underbrace{Pb(C_2H_3O_2)_2, PbO}_{\text{Basic lead acetate}} + \underbrace{K_2CrO_4}_{\substack{\text{Potassium} \\ \text{monochromate}}} + H_2O = \underbrace{Pb_2(OH)_2CrO_4}_{\text{Chrome red}} + \underbrace{2KC_2H_3O_2}_{\text{Potassium acetate.}}$$

In the manufacture of chrome red according to this equation the basic lead acetate must be made from a saturated solution of litharge in acetic acid, or by dissolving litharge in neutral lead acetate (59:100), and precipitating the boiling solution with a calculated quantity of potassium monochromate. On a large scale the process is by no means cheap, and the product lacks brightness. The same is the case if the basic lead salts obtainable by treating neutral lead acetate with caustic alkalies are treated in the same way. The entire loss of the acetic acid also makes the process expensive. This is shown by the following equation:

$$1.\quad \underbrace{2Pb(C_2H_3O_2)_2}_{\text{Neutral lead acetate}} + \underbrace{4NaOH}_{\text{Caustic soda}} = \underbrace{2Pb(OH)_2}_{\text{Lead hydroxide}} + \underbrace{4NaC_2H_3O_2}_{\text{Sodium acetate.}}$$

$$2.\quad 2Pb(OH)_2 + K_2CrO_4 = \underbrace{Pb_2(OH)_2CrO_4}_{\text{Chrome red}} + \underbrace{2KOH}_{\text{Caustic potash.}}$$

The whole of the acetic acid is lost as sodium acetate left in solution, while the chrome red remains as a heavy precipitate.

The process becomes more advantageous if, instead of the costly lead acetate, the basic carbonate (white lead), which is rich in lead oxide, is taken. On treating white lead with neutral potassium chromate at 100° C. it is entirely converted into a bright red basic lead chromate. The chemical reaction probably consists in two molecules of basic carbonate being decomposed by the monochromate to four molecules of neutral lead chromate, four molecules of potassium carbonate, and two molecules of lead hydroxide. By the aid of one molecule of potassium carbonate and water the neutral lead chromate is converted into the basic form, carbonic acid being liberated. Basic lead chromate falls down to the bottom as a dense precipitate, and the top liquor contains three molecules of potassium carbonate and one molecule of potassium monochromate abstracted from the neutral bichromate according to the equation:

$$1.\quad \underbrace{2(2PbCO_3.Pb(OH)_2)}_{\text{White lead}} + 4K_2CrO_4 = \underbrace{4PbCrO_4}_{\text{Neutral lead chromate}} + \underbrace{2Pb(OH)_2}_{\text{Lead hydroxide}} + \underbrace{4K_2CO_3}_{\text{Potassium carbonate.}}$$

$$2.\quad 4PbCrO_4 + 2Pb(OH)_2 + K_2CO_3 + H_2O = \underbrace{3Pb_2(OH)_2CrO_4}_{\text{Chrome red}} + K_2CrO_4 + CO_2.$$

That the chemical process really goes on in this manner can be seen by the changing colour of the mixture from the beginning to the final chrome red. The light yellow shade of the neutral lead chromate changes very rapidly at the high temperature to the dark orange chrome, and finally to the characteristic red of the pure basic lead chromate.

If the basic lead chloride (the preparation of which has been described on p. 133) be also taken into consideration, the manufacture of chrome red can be performed by the following methods:

(*a*) Precipitation of di-basic lead acetate with potassium monochromate.

(*b*) Decomposition of the neutral lead acetate with caustic alkali, and treating the resulting lead hydroxide with potassium monochromate.

(*c*) Treating the basic lead carbonate with potassium monochromate.

(*d*) From basic lead chloride with potassium monochromate or bichromate.

(*e*) Digesting the neutral or partly basic lead chromate (orange chrome) with caustic alkali (indirect method).

The methods *a*, *b*, and *c* are mostly out of use, and will therefore be only briefly discussed, since occasion for their use may arise in practice under certain circumstances.

Some general rules may be given here for beginners.

First of all, the quantity of water used in the process is a matter of the greatest importance with regard to the brightness of the chrome red, since as a decidedly crystalline body it will come out the lighter in shade the smaller the quantity of water used. To obtain a distinct shade (a matter depending entirely on the fineness of the crystals), the same quantity of water must always be taken, an allowance being made for the increase in the volume of the liquid by the condensed steam.

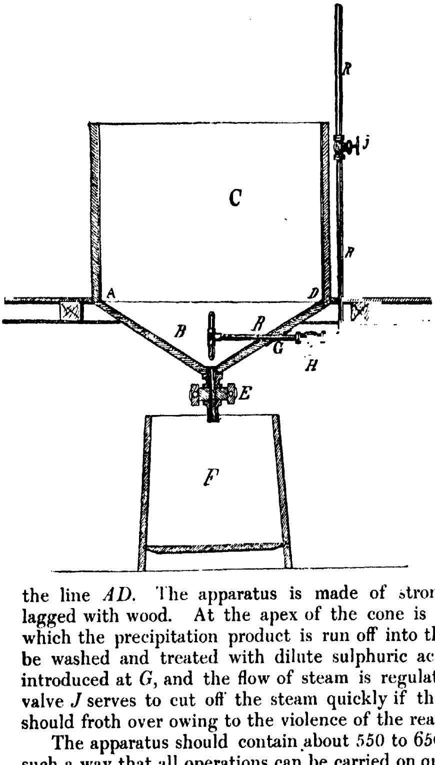
A frequent interruption of the crystallisation naturally disturbs the formation of the crystals, and therefore all superfluous stirring must be avoided during the manufacturing operations. A thorough mixing of the mass is only effected if absolutely necessary. Besides, the steam introduced into the liquid during the whole of the process causes sufficient motion, which also can be regulated by adjusting the steam valve according to requirements. In view, however, of this twofold effect of the steam, the steam pipes must be properly arranged. For instance, the steam must not be admitted into the tank from above, even if the pipe is led down to the bottom of the tank, since a considerable part of the rather heavy materials and precipitates may settle down on the periphery and be therefore excluded from decomposition. The reaction tanks must therefore be of such a form that the steam can be introduced into the middle of the bottom from below, and consequently a conical shape will be most suitable for the tank. The ascending steam keeps the liquid in constant motion, whilst the conical shape of the bottom precludes any premature deposition of the precipitates.

A further condition for obtaining satisfactory results is to operate at boiling heat, this being essential to the complete formation of the chrome. Low temperatures always result in a very fine-grained and therefore less bright product, similar to orange chrome. The same also occurs when the materials, *e.g.*, white lead, orange chrome, &c., are not in a sufficiently fine state of division; they must therefore be mixed to a thin paste before use, or employed in a freshly precipitated state.

The Manufacture of Chrome Red from White Lead

This process, by reason of its simplicity and reliability, is the one mostly used at present. On a small scale, for trial purposes, it may be carried out in the following manner. A small quantity of white lead in the state of paste corresponding to about 49 grms. of dry product is triturated with about 220 cc. of water in a mortar. The thin liquid mass is then poured into a strongly boiling solution of neutral potassium chromate without any stirring. This solution is prepared by dissolving 14 grms. of potassium bichromate in 500 cc. of water and neutralising with 13·5 grms. of crystallised soda (free from sulphate). The white lead being added, the mixture is allowed to boil strongly until it attains a deep violet shade (which takes about 8–10 minutes). The vessel is then taken away from the fire. The precipitate settles down very quickly; the yellow coloured top liquor is removed, and the colour is washed twice or three times with boiling water. The resulting rather dull looking product cannot yet be used as a pigment, but must be treated further with dilute sulphuric acid for conversion into true chrome red. For this purpose an acid obtained by mixing one part of concentrated sulphuric acid (sp. gr. 1·8426) with 10 parts of water is preferably used, 4 per cent. of the weight of the dry chrome red being usually taken. The acid is added slowly to the cold precipitate with constant stirring, whereupon the mass effervesces and turns bright red. To prevent the reaction extending to the formation of neutral lead chromate by an excessive addition of acid, the excess of acid must be neutralised with a dilute solution of soda, when the highest degree of brightness has been attained. It must be washed several times until the washings show a neutral reaction. The resulting very bright, dark red product consists of a mixture of basic lead chromate with very small quantities of lead sulphate of no influence upon the shade. The yield is about equal to the weight of the original dry white lead.

FIG. 78.



On a large scale the chemical process takes place in exactly the same manner. The vessel used for preparing the potassium monochromate, and the chrome red as well, consists of two parts (see Fig. 78), the cylinder *C* and the cone *B* fitting together water-tight in the line *AD*. The apparatus is made of strongly galvanised sheet-iron lagged with wood. At the apex of the cone is the cock *E*, by the aid of which the precipitation product is run off into the tank *F* underneath, to be washed and treated with dilute sulphuric acid. The steam pipe *R* is introduced at *G*, and the flow of steam is regulated by the valve *H*. The valve *J* serves to cut off the steam quickly if the liquor in the apparatus should froth over owing to the violence of the reaction.

The apparatus should contain about 550 to 650 galls., and is mounted in such a way that all operations can be carried on quickly and effectually.

The manufacture of dark chrome red is now performed in the following manner: 220 galls. of water are raised to boiling in the apparatus by means of steam, and 62 lbs. of potassium bichromate are added and carefully neutralised with 59 lbs. of crystallised soda. This latter must be added dry and in small quantities at a time, to prevent frothing over caused by the excessive liberation of carbonic acid. The end of the neutralisation can be very easily observed by the cessation of bubbles in the liquid. Steam is then turned on again, carefully at first, until at last the liquid boils, to expel the last traces of the carbon dioxide. The liquor being again at the boil, and in suitable motion, the thin paste of white lead (215½ lbs. of dry substance), previously ground with 55 galls. of water in an edge-runner mill, is added as gently as possible to the boiling solution of chromate, whereupon the chemical reaction is manifested by the immediate appearance of the orange red shade of the basic carbonate. With a little practice the progress and the end of the manufacturing process can be gauged by this gradual change of colour. No distinct rules can be given, much depending on contingencies, such, for instance, as the uniform admission of the steam, the method of adding the white lead (gradually or all at once), &c. If the whole operation has been properly carried out, the end can easily be judged by the dark red to violet colour of the mass; and at this point the decomposition product may be removed into the tank *F*. Should any irregularity occur during the process, the dark red to violet colour will not be formed, even after boiling for some hours, and the resulting chrome red will always be very pale in colour.

The removal of the product always needs special skill and experience, and therefore only an experienced man should be entrusted with this task. In consequence of its high specific gravity, the chrome red settles down very quickly on the cone, whereby the cock *E* very easily gets choked up. When this occurs it will have to be cleared by means of a stout iron wire—a very troublesome task—to enable the chrome red to run out. The cock should be opened as soon as the first particles of the chrome red settle down in the apex of the cone

The tank *F* is filled half full of boiling water, to wash out the chrome red the first time as quickly as possible. The tank may be of medium size, the quantity of chrome red being comparatively small, and any superfluous influx of mother liquor can be avoided by closing the cock *E* immediately the clear liquor is observed coming through. By using a somewhat larger tank, a second washing of the chrome red may be avoided. In treating the chrome red afterwards with sulphuric acid, the indicated strength of acid must be strictly maintained. In this case no further special precaution is necessary.

Instead of sulphuric acid, nitric acid may be employed, but not hydrochloric acid.

After the treatment with sulphuric acid, the chrome must be washed once with hot water, and is then spread on a linen filter and dried either in drying rooms or in the open air.

The clear yellow top liquor also contains potassium monochromate, and can be used for making cheaper brands of chrome yellow.

To manufacture other brands of chrome red the above proportions of the raw materials are retained, but the quantities of the liquid are changed, being decreased for light shades and increased for very dark (to violet) reds.

The Manufacture of Chrome Red from Basic Lead Chloride

On p. 134 (manufacture of chromes from basic lead chloride) it was stated that the formation of free caustic soda in this process enables basic lead to be made direct. This is now often done on account of the bright shades obtainable. The potassium bichromate as well as the monochromate can be used for this purpose, the latter, however, giving better results. The chemical reaction can be represented by the following equations:

1. With potassium monochromate, K_2CrO_4:

$$\underbrace{PbCl_2Pb(OH)_2}_{\text{Basic lead chloride}} + K_2CrO_4 = \underbrace{Pb_2(OH)_2CrO_4}_{\text{Chrome red}} + \underbrace{2KCl}_{\text{Potassium chloride.}}$$

2. With potassium bichromate, $K_2Cr_2O_7$:

$$2(PbCl_2Pb(OH)_2) + 2NaOH + K_2Cr_2O_7 = 2Pb_2(OH)_2CrO_4 + 2NaCl + H_2O.$$

In the latter process the potassium bichromate is converted by the caustic soda into a mixture of potassium and sodium monochromates, which act on the basic lead chloride in the same manner as the monochromate alone in Equation 1.

The following method is best. The mixture of the basic lead chloride and caustic soda is put into the boiling solution of potassium monochromate, containing a known quantity of the dry salt, heating being continued until the formation of chrome red is complete. The operation can be performed in the same apparatus as represented in Fig. 78, the directions with regard to the volumes of the liquid being also observed. Very dark, and therefore coarsely crystallised, brands of chrome red cannot, however, be obtained by this method, even when very large quantities of water are used. A further difference in the two methods consists in the fact that the chrome red in the latter process is formed immediately, and that any further treatment with sulphuric acid is superfluous. The washing, however, must be repeated several times, on account of the excess of caustic soda.

In using *potassium bichromate* the method is modified, inasmuch as the solution of the chromate is added to a basic lead salt, finely distributed in an ordinary tank, and afterwards slowly boiled. The decomposing action of the caustic soda on the potassium bichromate increases the duration of the process and entails the use of concentrated solutions of chromates. Dark shades of chrome red cannot, therefore, be obtained with this method.

The treating of the resulting chrome reds after washing is exactly the same as in the white lead method.

The manufacture of chrome red from basic lead chloride can be performed as described in the manufacture of orange chrome. On precipitating a solution of basic lead acetate (obtained from 100 parts of sugar of lead and 59 parts of litharge) with neutral potassium chromate, the dirty yellowish-brown precipitate mentioned on p. 145 can be observed, the structure and appearance of which change at an increasing temperature into a crystalline product of a bright dark orange red shade, which does not turn red even on prolonged boiling. If the washed precipitate of x basic lead chromate, however, is treated at boiling temperature with caustic soda its shade becomes considerably redder, and it shrinks, yellow sodium monochromate passing into solution. If on a further addition of caustic soda the intensity of the red colour does not increase, the chemical process may now be regarded as finished. The precipitate is then allowed to settle down; the top liquor is removed and the precipitate washed with hot water until the washing water contains no more sodium monochromate. When dry the product forms a very finely divided red powder, which, however, is of low intensity compared with that of the chrome red obtained by the white lead method. The whole process can be effected in a simple wooden tank (Fig. 1) heated by steam. The quantities of the liquors used have very little or no influence on the result, and if sometimes a brighter product is obtained the reason will be found in an accidentally greater purity of the raw materials.

The same method is used when lighter orange chromes or deep chrome yellows (*i.e.*, more neutral products) are employed as raw materials, except that a larger quantity of caustic soda is needed. However, the method will not furnish a chrome red of the same dark shade as that described above.

The manufacture of chrome red from pure lead hydroxide by precipitating a solution of sugar of lead with caustic soda has now being practically discontinued owing to the high cost. According to Gentele, a certain quantity of sugar of lead is dissolved in about an eightfold quantity of water in a copper vessel, and the boiling solution is treated with concentrated caustic soda until no more lead hydroxide is precipitated. Small quantities of potassium bichromate are then added with constant stirring until the settled precipitate is of a bright red shade. It is then removed, mixed to a paste with water, and allowed to stand a few days, after which time the top liquor is drawn off, the chrome red rewashed, filtered, and dried. A more suitable method is the precipitation with potassium monochromate, which gives a brighter but more coarsely crystalline product than Gentele's method.

Though chrome red very often occurs as a very dark, bright shade, this is of no use for many purposes in consequence of its gritty, crystalline form. Ground very fine, the colour is no longer dark red, but more or less orange yellow. Chrome red is really only useful in fresco painting as a substitute for vermilion. It can be easily mixed with oil, but separates again very quickly on account of its high specific gravity. Chrome red has the limited fastness of all lead colours.

Chrome red dissolves in dilute nitric acid to a clear red solution, in contrast to red lead and vermilion. Treated with sulphuric acid, the insoluble and sulphate is formed; with hydrochloric acid the almost insoluble lead chloride. All these solutions are green in colour.

Chrome red is sold too as *Persian red, Derby red, Vienna red, Victoria red, American vermilion*, &c. *Chrome red* or *purple red* is the name given to a precipitate obtained by treating a solution of a silver salt with potassium chromate. This precipitate is brighter than the lead compound, and of finer structure. The colour is not very fast, and is too dear for general use.

b. RED MERCURY COLOURS

Vermilion (*Zinnober, Vermillon, Cinnabar*)

Vermilion has been used as a colour from the earliest times. As far back as 400 years B.C. it was mentioned as a colour used by the Egyptians for painting pictures of the gods ("Sapienia," chap. xiii. 14). According to D. Chimchi, the schaschar of the ancient Hebrews, used for similar purposes (Jeremiah xxii. 14, Ezekiel xxiii. 14), was nothing else than vermilion.

According to this author, vermilion was used as a pigment 600 years B.C. It must, however, be assumed that the Assyrians, and probably still earlier the Chinese, already used vermilion as a colour. Pliny mentions vermilion under the name "minium."

Vermilion is a compound of mercury and sulphur, of the formula HgS, and is found native in many places. The best known deposits are at Almaden and Almadenjas, in Spain, and Idria, in Austria. In the vicinity of the Rhine (Bavaria), in Westphalia, in some parts of Austria (Styria, Bohemia, Hungary, &c.), in the Urals, in China and Japan, in Mexico and Peru native vermilion is also found in more or less considerable quantity, and of variable purity. The deposits in California are of great importance. Vermilion is principally found as beds and lodes in the crystalline slate rocks, &c., and sometimes in the shape of loose round lumps in secondary deposits. The native vermilion is known in commerce as *cinnabar* (mercury blende).

Whilst the ancients always used this native vermilion, it is only employed on an extremely small scale at present. Most of the technically used vermilion is manufactured, and is of a far brighter shade than the native variety, and is even then of only moderate brightness. Before use the latter must be wet ground, dried, and sifted.

The manufacture of vermilion, like that of nearly all mineral colours, has been kept secret by the manufacturers until recently. Nevertheless the process is a very simple one, and any technical difficulties now experienced are solely due to the high price of mercury, and especially to its poisonous properties, necessitating special precautions and highly economical methods.

Two principal methods of manufacturing vermilion are now employed :

1. The *dry method*, in which the raw materials are used solely in the dry state ; and
2. The *wet method*, in which at least one of the materials is used in a dissolved condition.

Vermilion was manufactured by the first method until within the last few decades, especially in Holland, but at present the method is only used in Idria, and even there with some important improvements (Austrian vermilion).

The so-called wet method, founded on a purely scientific basis, is the best, and as it has become an almost exclusive speciality of the German colour industry it may justly be termed the *German method*.

Dry Method

The manufacture of vermilion in the dry way rests upon the property of mercury for combining chemically with sulphur by simple mixing. At first a powdered black mass is obtained, the *amorphous* black sulphide of mercury, forming the raw material for the manufacture of *crystalline* mercury sulphide, the true red vermilion. Both modifications have the same chemical composition, HgS.

The conversion of the black modification into the red one can be effected in various ways. In the dry method it is performed exclusively by sublimation at a definite temperature.

The dry method is therefore divided into two stages, viz.:

1. The production of the black mercury sulphide.
2. The sublimation to red sulphide (vermilion).

These two stages are followed by a third, the technical finishing of the sublimed product to form the commercial article.

Whereas the two first or principal stages differ in Dutch and Austrian practice both in the apparatus and the *modus operandi,* the finishing process is the same in both cases.

The *Dutch method* being a very imperfect one, according to present-day notions, may be described shortly as being the pioneer process leading up to the latest methods.

The black sulphide is obtained by placing metallic mercury into melting sulphur, and the mixture is stirred until chemical combination occurs. A simple iron pan is used—a primitive and somewhat dangerous process, not unattended with risk of explosions. To avoid this danger it is advisable to add the mercury in small portions at a time, and to moderate the fire during the operation, so that the sulphur has just the suitable consistence for the mixing process. When all the mercury has been added—according to the Dutch recipe, 18 parts of sulphur are generally taken to 100 parts of mercury—the black mass in the pan is constantly stirred with an iron spatula until an absolutely uniform powder is obtained. This operation is rather difficult, and must be performed with great caution; on this depends not only the quantitative yield, but also the brightness of the vermilion.

The second stage is carried on in special pots, placed in specially constructed furnaces, so that about two-thirds of the pot is exposed to the direct heat of the fire. The charge is added in small portions in this case also. The pots are of earthenware, and oval in shape. The larger end is placed below, forming the bottom of the pot, and the pointed end is cut off, the opening thus left being covered with a somewhat larger cast-iron plate. The charge of black sulphide is added when the pots have been heated to redness as slowly as possible in order to prevent breakage. As the portions of sulphide are introduced they burn with a bluish-white flame, which is allowed to subside before a fresh portion is added. The operations can, however, be accelerated as the prescribed quantity of mercury is nearly exhausted, since by this time the temperature in the pot has increased and the burning of the sulphide proceeds more rapidly. The quantity of the charge depends, of course, in the first place on the dimensions of the pots, and must be ascertained by trials beforehand. The most usual dimensions of the subliming pots are 24 to 26 ins. high, and average about 16 ins. across the middle.

The whole of the charge being added as described above, and the sulphur burned until the white flame has nearly ceased to issue from the pot, this latter is covered with the above-mentioned iron plate, and the temperature is rapidly increased for the process of subliming the vermilion. During this process, which requires about thirty-six hours of uniform heating, the plate must be uncovered a little from time to time to avoid a premature suppression of the sulphur flame. The mass must be stirred up quickly and thoroughly well by aid of an iron rod each time. The sublimation can be considered finished if on uncovering the iron plate no more flame can be observed, and the plate itself shows a considerable crust of sublimed vermilion on its under side.

Heating is then stopped, and the pots allowed to cool in most cases. To be able to collect the whole quantity of vermilion the pots must be broken, the sublimed vermilion being carefully removed from the broken pieces. If properly managed, the yield will be 3 to 4 per cent. less than the total weight of the raw materials used. The further finishing of the resulting vermilion (vermilion in pieces) will be described later on, in the manufacture of vermilion by the Idrian method.

The *Idrian method* utilises the improvements of theoretical research and employs the most suitable apparatus both for reducing the loss of materials and vermilion as well as to minimise the dangerous character of the manufacture. This method therefore endeavours, not always with success, to avoid the faults of the Dutch process. The first stage, viz., the production of the black sulphide of mercury, is based on the mixing of the raw materials (sulphur and mercury) in accordance with theoretical research and the maintenance of economy, so far as is practically feasible. The same is the case with the subliming pots used in the second stage, these being provided with distillation hoods and receivers.

The proportions used in mixing the raw materials differ somewhat from the theoretical quantities, 20 parts of sulphur and 105 parts mercury being taken. The mixing is effected in rolling casks, provided on the inside with narrow longitudinal ribs, and supported on a common frame. The barrels are rotated by a train of pinions similar to the arrangement shown at Fig. 68, the ribs facilitating the mixture of the raw materials. The barrels are made of elm, and provided with iron hoops. In large works as many as twenty barrels are used, all mounted (see the grinding of soda ultramarine green) on strong frames driven from a common shaft.

The barrels make fifty to sixty turns per minute, and are mounted in pairs running in opposite directions. The duration of this process is about three hours. The product is merely a mechanical mixture, from which free mercury can be separated by strong pressure. To convert this mass into a chemical compound the mixture must be heated at about 150° C., the same result being attained as in the Dutch process—ignition of the surplus sulphur, with occasional detonations. During the heating the black mixture turns into a dark violet, rather soft powder.

For obtaining a proper mixture the quality of the powdered sulphur is of special importance, since the mercury will only combine when the sulphur is applied in a coarsely powdered form. Conversely, if too finely powdered the sulphur floats on the metal. Therefore the speed of the barrels must be regulated accordingly. The most suitable gauge of sieve for sifting the sulphur beforehand must be ascertained by experiment.

During the rotation the mixture in the barrels will become rather warm (25° to 30° C.), and the increase in temperature will be the greater the warmer the working rooms are. The duration of the mixing process varies inversely with the temperature. The mixture being so far complete that a sample no longer reveals globules of free mercury when examined with a magnifying glass, the barrels are stopped, emptied, and the resulting mixture divided into portions of 26½ lbs. each and placed in suitable earthenware pots. The weight of charge put into the rolling casks depends, of course, on their dimensions.

The *sublimation process* of the black mercury sulphide is carried on in a kind of reverberatory furnace, heated from a wood or coal fire. Several furnaces of this kind are generally in work at the same time. The pear-shaped sublimation pots of cast iron are arranged in sets of six, mounted on suitable strong iron frames, and charged with equal portions of the mixture from all the rolling casks, in order to prevent the formation of sublimates of different shades. The pots are large enough to take 130 lbs. of the mixture each, and still leave enough free space to prevent any trouble during the subliming process. This process has three different stages—the *vaporisation*, viz., the chemical combination of the mercury with the sulphur; in the second stage the distillation hoods and receivers are displaced, and is followed by the *real subliming process*, in the course of which the red compound, vermilion, is produced.

When all the pots have been charged with the raw mixture the sheet-iron hoods (weighted with brick) are put on, and the earthenware receivers attached. The joints are not heated during this stage. To minimise the danger arising from the detonation the pots are heated up in pairs, and when the sulphur has ignited the heating of the following pair is commenced, and so an ignition occurs in a very short time, so that the first stage is not a very long one. When the flame issuing from the pots has diminished, and no more whitish fumes of sulphur dioxide are observed, the process can be considered finished, and as soon as this is the case with all the pots the following operation may begin. The iron hoods are taken away, and replaced by others of earthenware. All the joints are luted with earth, or preferably fire-clay. The furnaces are now heated, and the draught arranged so that all the pots are bathed by the flame. As the heat increases, and generally in a short time, the sulphur re-ignites, and burns at first with a small flame inside the pot. In proportion as the temperature increases, the flame of the sulphur becomes larger, so that after about three hours it extends beyond the neck of the hood, whereupon the receivers are attached, in order to collect the distilled sulphur. In many works an earthenware pipe 20 to 30 ins. long is arranged between the hood and the receiver to facilitate cooling. All the joints must be luted with earth or clay. The receivers are provided with a tubulus fitted with a clay plug, to regulate the escape of the sulphur vapour, so as to relieve the pressure of the gases. When heating is so far advanced that a constant flame issues from the tubulus it is a sign all the sulphur condensed in the pipes and receivers is consumed, whereupon the next process, the real *sublimation of the vermilion*, will begin. The tubulus is now closed and luted with clay. To prevent any bursting of the lutes, which often happens with loam at the higher temperature, and consequently a loss of vermilion, the joints must be kept moistened during the whole process of sublimation. If all goes well and no interruption of the heating occurs, the process can be considered as finished in about four and a half hours, calculated from the luting of the tubulus. The end point is revealed by the appearance of a small flame at the joints between the pot and the hood, the luting having been partially removed for that purpose. The fire is then drawn, and the distillation pots and receivers allowed to cool. The bulk of the sublimed vermilion will be found in the receivers in a specially pure state and of bright shade. A less pure sublimate will be found in the pipes and on the inside surface of the hoods, and this portion must be resublimed, or else added to the following charge of black sulphide of mercury to be heated for sublimation.

The subliming apparatus being dismounted, the receivers must be broken, so as to obtain the vermilion without any loss. The sublimed mass in the pipe is scraped out with an iron rod, and these pipes, consequently, can be used several times over.

A simpler plan, of course, is to remove the sublimed product from the hoods with a stiff brush. The product obtained in this way is more pulverulent, and is sometimes called *clean vermilion,* to distinguish it from the *vermilion in pieces.* A properly conducted operation will yield as "Vermilion in pieces," about 70 per cent. in the receivers, about 25 per cent. in the pipes, and 2 per cent. in the hoods. A small residue in the pots consists of metallic sulphides from impurities in the mercury.

The *third stage* (common to both processes) of the manufacture of vermilion in the dry way is the grinding and finishing of the "vermilion in pieces" obtained by sublimation. The grinding is carried on under water, the wet mill of medium size represented in Fig. 9 being the best. The levigation process is precisely the same as already described (*q.v.*). The only point to be observed is that the "vermilion in pieces" requires four or five grindings to furnish a suitably fine product. In consequence the resulting colour is always of a lighter shade, but no brighter in appearance. There is, therefore, a certain limit to this manipulation, which, however, by thorough attendance and by practical experience can be modified considerably, to the benefit of the product and duration of the process.

The *refining* of the washed vermilion is to remove the impurities—black sulphide of mercury, free sulphur, &c.—which remain in the vermilion in spite of all the care taken during the subliming process, thus influencing considerably the brightness of the shade. The appearance of the commercial article depends, therefore, on this refining process. It consists in treating the ground vermilion with alkaline solutions, in which the impurities mentioned are easily and completely soluble. This operation is performed at boiling temperature, and is followed by a thorough washing of the vermilion. By means of several washings the dissolved impurities and the excess of the alkaline liquor are entirely removed. In the Idria process solutions of potash, either made in the works by treating suitable ash or from purchased alkali, are used. The concentration of the solutions varies according to the vermilion to be treated. For bright red vermilion a solution of 10° B. is quite suitable; for darker shades, however, solutions of 11° to 12° B. are absolutely necessary. The procedure is just the same in all cases. The ground vermilion is added to the alkaline solution in a suitable iron vessel, thoroughly well stirred, and the mixture is kept at boiling temperature about ten minutes. The colour is then allowed to settle down, and the top liquor syphoned off. It mostly contains potassium pentasulphide, besides small quantities of dissolved mercury sulphide. The vermilion in the vessel is removed and washed in a tank several times with boiling, and finally with pure cold, water in the usual manner. The washing can be considered as finished when the last washings are absolutely clear (not milky), or no longer show an alkaline reaction.

The washed vermilion is then dried on handy enamelled iron pans, at 70° to 75° C., in drying-rooms. The lighter shades are liable to cake—a defect easily remedied by working the dry mass with suitable wooden rolls. The vermilion must generally be sifted once more before it is ready for sale.

German or Wet Process

For the manufacture of the vermilion in the wet way various methods are used, all of them furnishing a product of a much brighter appearance and purer shade than that from the sublimation process, and scarcely inferior to the true Chinese vermilion, prepared by a secret process.

According to *Kirchhoff*, the older method is as follows: 300 parts of mercury are mixed very intimately with 68 parts of sulphur until no more globules of mercury can be detected in the mixture, and a perfectly homogeneous mass is obtained. At the end of this operation a small quantity of caustic potash must be added, the resulting black mercury sulphide being treated, for conversion into the red modification, with concentrated caustic potash, the colour changing slowly to a brownish red, and then more quickly to a scarlet red. The mass should always be kept in a damp state, so that the evaporated water must be replaced from time to time. The addition of water is kept up until the mass has gradually become red all through. The temperature is then increased (with continued stirring), but only as long as the intensity of the shade continues to brighten, and the mass has become gelatinous. This state being attained, the mass is removed from the fire and allowed to cool slowly. If the heating be prolonged any further the colour would revert to a brownish red, which, of course, has to be avoided. This constitutes a certain defect of the process, and Kirchhoff therefore proposed to remove the mixture from the fire immediately after the appearance of the red shade, and to digest it for several days at a moderate temperature. In this way the bright red shade of the product is obtained without any risk of discoloration. The vermilion is then washed several times with a very dilute solution of caustic potash, and afterwards with pure cold water. The washing water contains dissolved mercuric sulphide, which separates out on prolonged standing, and would therefore contaminate the vermilion if the washing were conducted with pure water from the beginning.

In consequence of the uncertain result, the Kirchhoff method did not find any practical application, and was quickly superseded by *the Döbereiner* method, afterwards improved by *Th. Martins*. This method rests upon the direct transformation of the metallic mercury into red mercury sulphide by the aid of potassium pentasulphide, K_2S_5.

$$\underbrace{K_2S_5}_{\text{Potassium pentasulphide}} + \underbrace{Hg}_{\text{Mercury}} = \underbrace{HgS}_{\text{Vermilion}} + \underbrace{K_2S_4}_{\text{Potassium 4. sulphide}}$$

The potassium pentasulphide is obtained in the purest state by melting potassium monosulphide, K_2S, with the corresponding quantity of sulphur, and forms a dark brown leather coloured mass, smelling like sulphuretted hydrogen. It readily deliquesces in the air to yellow liquor. The potassium monosulphide is obtained by heating potassium sulphate with carbon.

The pentasulphide is manufactured by mixing and fusing potash (potassium carbonate) with the corresponding weight of sulphur in large crucibles. At the beginning the mass froths up, owing to the escape of carbonic acid, but soon melts, and is poured on to iron plates, whereupon it is allowed to cool. The potassium pentasulphide obtained in this way still contains considerable quantities of potassium sulphate and sulphide.

In the *Döbereiner process* pure metallic mercury is mixed at a moderate temperature with a concentrated solution of potassium pentasulphide until a dark red powder is obtained, this being then separated by decantation and converted into true vermilion by treatment with concentrated caustic potash.

The digestion is effected at about 40° to 50° C. in iron vessels, and is continued till the brightest shade of the compound is obtained. The mass is then allowed to cool, and washed in the usual way. Here also an excessively high temperature causes the colour to turn brownish red. This defect, however, can be avoided, according to *Martins*, by filling the components into strong glass bottles and heating them on specially constructed swinging apparatus. The formation of the vermilion is greatly furthered by the uninterrupted shaking of the mixture, and proceeds without any artificial heating, whereby all danger of the transformation into the brown-red modification is prevented. The operation is, however, a tedious one. As may be seen from the equation, the advantage of this process rests upon the fact that no other material except mercury and sulphur are used, and that the used raw materials can be recovered from the mother liquors separated from the vermilion. For this purpose the solution of potassium tetrasulphide is boiled, and finely ground sulphur is added slowly until saturation (viz., potassium pentasulphide) is obtained. The end of the reaction can be easily observed by the violent ebullition of the liquor and the formation of bubbles on the surface.

The increased weight of product obtained by this method is another advantage, as compared with the sublimation process. With good management the yield will be 110 per cent., the loss of mercury taking place in the dry method being absolutely precluded. It is, however, necessary that the metallic mercury should be perfectly free from any other metal, otherwise the sulphides of the admixed metals would also be formed and the shade of the vermilion adversely affected.

There are several other methods for manufacturing vermilion by the wet way, of which the following may be mentioned:

O. Hansamann (Wagner, *Jahresber.*, xxi. 619) uses mercury ammonium chloride, NH_2HgCl, a white precipitate, obtained by precipitating a mercury chloride solution with sal ammoniac. The flocculent precipitate is treated with a highly concentrated solution of sodium hyposulphite until entirely dissolved. On heating this solution a certain time, the vermilion begins to separate. The presence of ammonia and ammonium chloride in the solution seems to greatly influence the appearance as well as the formation of the vermilion. The temperature also plays an important part in the reaction, for the lower the temperature the lighter the resulting product. The brightest shade is said to be obtained at 70° to 80° C.

According to *Raab*, red vermilion is obtained by heating calomel (mercurous chloride) in a powdered state with a solution of sodium hyposulphite to boiling. The black sulphide of mercury is separated from the top liquor and heated with a concentrated solution of potassium pentasulphide under constant stirring, whereby this red modification—viz., the vermilion—is formed. After recooling, the resulting product is washed and dried.

Vermilion can be prepared electrolytically, but this method has not yet been adopted in practice.

Vermilion is the brightest red mineral colour known, and is on this account very largely used. In consequence of its high price it is not much used as an ingredient of paints—viz., for ordinary work—having been almost entirely displaced by the aniline lakes, the so-called vermilionettes. Vermilion has the defect of turning black in the light after a certain variable time, many vermilions keeping their bright red colour for years, whilst others change colour in a few months. The change is believed to be due to the conversion of the crystalline modification to the amorphous form, but this lacks confirmation. Many circumstances rather favour the assumption of a reduction of the sulphide to a lower state, sulphur being set free, the change being accelerated by the presence of certain impurities.

Pure vermilion is insoluble in alkalies or in dilute acids, and differs, therefore, from the imitation vermilions (vermilionettes), which also part with most, or all, of their colouring matter on treatment with alcohol. When heated, vermilion changes colour, first to a bluish shade, afterwards to brown, and finally to black, igniting and burning with a bluish flame until almost completely volatilised. The residue should exceed 0·4 per cent. Adulterants such as red lead, ferric oxide, barytes, brick-dust, &c., remain as a residue, mostly without change. This heating test must be applied on a porcelain plate, platinum being easily injured by amalgamation, resulting in fusion. A mixture of nitric and hydrochloric acid dissolves vermilion and forms a colourless solution. Bromo-hydrochloric acid has still greater solvent power.

Vermilion is one of the best covering colours, requires only a small amount of vehicle for paints, but easily separates. It also dries badly.

When rubbed in a damp state on a polished brass plate a black tarnish is formed.

Carmine-vermilion is the trade name sometimes applied to a mixture of finely levigated ferric oxide (colcothar) with true vermilion.

Brilliant Scarlet (HgI_2; *Mercury Iodide, Scarlet Red, Iodzinnober, Ecarlat*)

The compound of mercury with iodine has a beautiful red shade, but the hopes to which this product gave rise have not been realised, the price being too high, and its place filled by the aniline lakes already mentioned, so that it is now rarely used as a pigment.

The colour can be obtained by precipitating an aqueous solution of mercury chloride with one of potassium iodide. The scarlet red precipitate is washed, filtered, and pressed. The other recipes known are partly too complicated, partly too expensive, for description here.

Brilliant scarlet is not fast to air. In the light it very soon turns yellow, then brown, and finally black. As a water colour it is absolutely useless. Ground in oil it is more permanent, but it is said to disappear absolutely when heated gently for some time. It dissolves in potassium iodide to form a colourless solution.

Mercury Chromate (Hg_2CrO_4)

On treating dissolved mercurous or mercuric salts with a solution of potassium chromate bright red precipitates are obtained, similar to vermilion. This colour is best obtained by precipitating mercuric nitrate with potassium chromate, followed by washing. The mercury chromate, both in the dry state and when ground in oil, changes very easily, and is rapidly blackened by sulphur fumes. It darkens, too, very quickly when ground in oil, and is therefore of no technical value.

c. RED COPPER COLOURS

Copper Ferrocyanide (Cu_2FeCy_6; *Vandyke Red*)

This compound is of a dark violet-red shade, with a brown tinge. It is still sometimes used as an artist's colour, but is very seldom found in trade as a material for paint. The shade can be imitated cheaply and very easily with red ferric oxide colours, and, indeed, Vandyke red has no specially advantageous qualities. The pigment is obtained by treating an aqueous solution of copper sulphate with one of potassium ferrocyanide, a violet-red precipitate being formed, which is then washed and dried. The copper sulphate must be absolutely free from iron, to prevent the formation of Prussian blue; the Swedish sulphate is therefore generally used.

According to another recipe, 37·5 parts of potassium ferrocyanide are dissolved in hot water, 3·75 parts of sal ammoniac being then added, and the mixture, after being allowed to stand for some time, is precipitated with a solution of 23 parts of copper sulphate, with continued stirring. The precipitate must be washed several times, and afterwards dried.

d. RED ANTIMONY COLOURS

Antimony Vermilion ($Sb_6S_6O_3$; *Antimonzinnober, Vermillon d'Antimoine*)

This pigment also has lost much of its former importance, being replaced by aniline lakes of much greater brightness and permanence. Its preparation will therefore be only briefly described here.

The method of *Kopp* (*Dingl. Journ.*, cliv., p. 296) for making antimony vermilion rests upon the decomposition of the calcium hyposulphite with antimony chloride. The resulting clear liquid is heated to 60° to 70° C., whereupon the red colour separates slowly as a fine soft powder. The operation can be made continuous by using a series of tanks, each holding 450 to 650 galls. The tanks are placed about 40 ins. from the ground, and provided with steam heating coils to prevent any contact of the steam with the solution, and consequently any increase in the volume of the liquid by condensed steam. The tanks are disposed so that the top liquors can run into a common collecting tank below.

The tanks are filled seven-eighths full with a solution of calcium hyposulphite, the solution of antimony chloride being added in small portions—about ½ gall. at a time. A white precipitate is formed, which, however, dissolves immediately on stirring the liquid. The addition of antimony chloride is discontinued when the white precipitate becomes persistent, forming a slight cloudiness in the liquid. This must be removed by adding calcium hyposulphite again until the solution is perfectly clear. The temperature is brought to 60° to 70° C. by turning on the steam, and stirring is continued, the liquor gradually turning straw yellow, then lemon yellow, and finally orange. At this moment the steam is stopped, but stirring is continued for a short time. The heat of the liquid is now enough to finish the reaction—viz., to give the brightest shade to the precipitate. By continuing the heating the colour would turn from orange to a carmine red, and finally to brown, or at last black. Consequently all shades from orange to brown-black can be obtained by regulating the temperature.

When cold the top liquor is removed into the collecting tank, already supplied with calcium sulphide. The sulphurous acid of the top liquor is combined by the calcium sulphide, forming calcium hyposulphite, which can be used for making antimony vermilion. In this regeneration process an excess of calcium sulphide must be avoided, since it will form with antimony chloride the common orange-coloured antimony sulphide, remaining admixed with the antimony vermilion and impairing its brightness.

The regeneration process, however, can be easily controlled by the iron present in the antimony chloride. All iron in the top liquor of the antimony vermilion being present as ferric chloride, this latter forms with the calcium sulphide a precipitate of black iron sulphide, which only disappears when an excess of sulphurous acid is present, forming ferrous hyposulphite. When this occurs more calcium sulphide must be added, until the precipitate of iron sulphide reappears and persists. This is then allowed to settle down and the clear top liquor taken away. This latter must have a perfectly neutral reaction before it can be used again.

During the time the precipitate in the first tank is settling down the same manipulation is performed on the second, and then on the third tank. The first tank will meanwhile be emptied, and the liquid reconverted into calcium hyposulphite for use over again.

The resulting antimony vermilion is washed several times with tepid water, filtered, and dried at 50° to 60° C. It is not a fast colour, being unable to resist even very dilute acids, or more especially alkalis, so that its application is very limited. At a higher temperature antimony vermilion is converted into antimony sulphide, and blackens even when heated gently.

e. RED COBALT COLOURS

The red- or pink-coloured cobalt compounds are more of scientific interest, being too dear for technical use. According to *Gentele*, when cobaltous arsenate (*chaux métallique*), of a violet shade, is very strongly heated for some time a violet-coloured mass is formed, representing, when finely ground, a pink-red powder. The colour is said to be less bright than the madder lakes, but faster to light. The same colour was formed by Gentele from the same arsenate with a little borax, in a porcelain kiln, as a violet mass, giving the same pink-red powder when finely ground.

According to *Salvetat,* pink cobalt is obtained on precipitating a solution of a cobaltous salt with sodium phosphate. The dried precipitate is pink, changing to violet when heated.

Cobalt magnesia pink is obtained when finely powdered precipitated magnesium carbonate is mixed to a thin paste with a solution of cobalt nitrate. The mixture is then dried and heated in crucibles, a bright pink-red pigment being obtained.

The metal *tin* gives *chromium stannate.* According to *Gentele,* a solution of bichromate, chalk, and powdered quartz are mixed together to a homogeneous paste, dried, and raised to white heat. The melt is washed, and the residue, the so-called *pink colour,* is used as a pigment, especially for artist's colours, serving here as a substitute for madder pink. The shade can be varied by altering the proportions of chromate and lime.

According to *Schwarz,* gelatinous silica mixed with potassium bichromate and calcined also gives a bright pink colour.

Purple of Cassius is not a true pigment, but is used chiefly for ceramical purposes—painting on porcelain and enamel. It consists of gold stannate, or, according to others, of stannic acid containing a red-coloured modification of gold in mechanical suspension. The manufacture is rather complicated. *Müller* obtains a *gold purple* by moistening calcined magnesia with gold chloride. The yellowish-coloured powder is dried and calcined, turning thereby to a bright carmine shade. According to the same author, an *alumina purple* can be obtained on treating alkaline solutions of alum with gold chloride. This product has more covering power than the magnesia purple, but has a more violet tinge.

BROWN MINERAL COLOURS

Owing to the abundance of powerful brown minerals of such soft texture that they can be easily prepared by mechanical treatment for painter's, artist's, paper stainer's, and litho printer's colours, the manufacture of artificial brown mineral colours is unprofitable and superfluous. Greater importance attaches to the manufacture of brown lakes by the coprecipitation of red, yellow, or orange aniline dyes with blues or greens. Lakes of this class are specially used for manufacturing wall and fancy papers, and on account of their agreeable and bright shades are often preferred to the earth colours.

The various proposals made to produce brown mineral colours artificially have not been adopted in practice, and therefore need not be discussed.

Prussian brown is calcined Prussian blue, but seldom used. *Chrome brown,* obtained by precipitating potassium bichromate with cupric chloride, is a warm, deep brown, sometimes used as a water colour.

Copper brown is obtained on precipitating a mixture of copper sulphate and magnesium sulphate with potassium carbonate, the washed precipitate being then heated.

Cobalt brown is formed by calcining a mixture of ammonium sulphate, cobaltous sulphate, and ferrous sulphate.

PART III

THE RAW MATERIALS USED IN COLOUR MAKING

MANUFACTURE, PROPERTIES, AND QUALITATIVE EXAMINATION

SINCE the practical and advantageous application of chemical reactions is usually the basis of the manufacture of mineral and lake colours, a thorough knowledge of the raw materials used for this purpose and of their chemical and physical qualities is essential. Without this knowledge it would be quite impossible to understand the technical operations or their real purpose, the manufacture of the coloured precipitates, or to utilise the products thereby formed. The chemical reactions change the raw materials into entirely new bodies, which either form the colouring principle of the pigments or else their basis, or both together. It is therefore very important for every one in the colour-manufacturing industry to know exactly the peculiarities of the raw materials. The properties of such products, which constitute real colours themselves—*e.g.*, red lead, lead chromate, copper hydroxide, &c.—have already been dealt with in the second part, on the manufacture of these colours. The description of such bodies, however, as form the basis of pigments, and formed simultaneously with them (as is mostly the case in the manufacture of lakes), or mechanically admixed at the moment of formation, will now be given, together with the true raw materials and their properties. This arrangement remedies a defect of the older text-books on colour-making, and gives readers who lack chemical knowledge a good opportunity of gaining further instruction. Nevertheless we shall confine ourselves to points of a certain importance in the manufacture of colours, and at the same time to the compounds used in making the lake pigments to be described at a later stage.

a. ALUMINIUM COMPOUNDS. (ALUMINA SALTS.)

Aluminium Sulphate ($Al_2(SO_4)_3 + 18H_2O$; mol. w., 664·8)

This compound is found native in considerable quantities as so-called *halotrichite* and *aluminite* (Websterite), the latter with only 9 molecules of water of crystallisation. The artificially produced pure aluminium sulphate crystallises in thin and soft nacreous needles or leaves, and does not change in the air. Aluminium sulphate is readily soluble in hot water, more sparingly so in cold water, and loses its water of crystallisation when heated.

Aluminium sulphate is manufactured on a large scale by heating clay free from iron with sulphuric acid. It is very often used instead of alum, and is put on the market in large square blocks of a white shade, sometimes known as "concentrated alum." The production of aluminium sulphate from clay (alumina, cryolite) or bauxite will be described later on, under the manufacture of alum (*q.v.*). When made from clay or alumina the diluted solution of aluminium sulphate is treated with potassium ferrocyanide, whereby all the iron present is precipitated as Prussian blue. From cryolite aluminium sulphate is obtained by treating the alumina (precipitated from the sodium aluminate) with sulphuric acid (of 52° B.), and heating to 80° to 90° C. The saturated solution is allowed to stand for a certain time, and afterwards concentrated in copper vessels until the mass melts. In this state it is removed with suitable copper ladles into flat, square copper moulds, where it sets hard.

Alum ($Al_2K_2(SO_4)_4 + 24H_2O$ or $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O$; mol. w., 948)

Alum is chiefly found in volcanic countries in the form of an efflorescence on "alum shale" (keramohalite). In this form it is, however, of no practical importance, all the alum used being manufactured artificially. According to *E. Fischer,* the minerals suitable for this purpose may contain aluminium only, like bauxite or cryolite, or contain the elements necessary for the formation of alum or aluminium sulphate, such as alunite, &c.

Alunite may be regarded as consisting of 1 molecule of alum + 2 molecules of aluminium hydroxide: $K_2SO_4 + Al_2(SO_4)_3 + 2Al_2(OH)_6$. At a slight red heat it is converted into a compound, from which the alum can be extracted with water, the portion left uncombined by the sulphuric acid remaining undissolved. Without previous heating (to 500° C.) the water will not dissolve alum at all from the crystallised alunite. Alunite is found at *Tolfa* (Italy) and *Munkács* (Hungary). The alum found at Tolfa is known in the trade as *Roman alum.*

The most important raw material for the manufacture of alum, however, is *alumina,* a clay mixed with pyrites and bitumen, and *alum-shale,* a clay shale also mixed with pyrites, but brown in colour from lignite.

These minerals are left for a certain time, according to their structure, to effloresce, or else roasted. In the former case the iron sulphide is oxidised by the oxygen of the air and by water to ferrous sulphate and free sulphuric acid, the latter forming aluminium sulphate with a corresponding quantity of clay: $FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4$. The effect of the roasting process is quite similar. The iron disulphide (FeS_2) forms sulphurous acid and iron monosulphide (FeS). Whilst the sulphurous acid decomposes the clay, forming ammonium sulphite and sulphate, the iron monosulphide is converted into ferrous sulphate, and this latter into ferric sulphate. Sulphuric acid becomes free, and partly decomposes the clay afresh.

The effloresced or roasted alum ores are levigated in large tanks, arranged in terraces one below the other in such a way that the resulting solutions run from one tank to the next below, and from this again to one still lower, and so on until the solutions, becoming progressively stronger, reach a common collecting tank. They have then a specific gravity of 18° to 20°, seldom 20° to 25° B. The impurities are then allowed to settle down as a brown red sludge (iron sludge). The clarified solutions are afterwards run into the so-called "boiling house" to be concentrated. This latter operation is performed in leaden pans, cast-iron vessels, or bricked pans with a flat vault, and heated by the direct influence of the fire on the surface of the lyes, or by means of inserted pipes. Since these solutions generally contain much ferrous sulphate, many alum works, therefore, also manufacture ferrous sulphate.

If the solutions are concentrated to a specific gravity of 1·4, the basic ferric sulphate separates out, and the solution turns a reddish yellow colour. After this clarifying process the solution is led into the precipitation tanks (jigs), where precipitation is effected by the addition of a potassium or ammonium salt. 100 parts of aluminium sulphate must be precipitated with 43·5 parts of potassium chloride, or 50·9 parts of potassium sulphate, or 47·8 parts of ammonium sulphate. The alum precipitates as a fine crystalline powder (alum powder), which is washed several times to remove any adherent mother liquor. This manipulation is now mostly effected in centrifugal apparatus. The alum powder is then again brought into crystals, the ordinary trade form.

In the manufacture from cryolite (sodium aluminium fluoride) this latter is mixed with calcium carbonate and heated. Carbonic acid escapes, and soluble sodium aluminate, besides insoluble calcium fluoride, is formed: $Al_2Na_6Fe_{12} + 6CaCO_3 = Al_2(ONa)_6 + 6CaFe_2 + 6CO_2$. After levigating the sodium aluminate the carbonic acid obtained and collected from the previous melting process is returned into the solution, aluminium hydroxide being then precipitated. After some standing the top liquor, containing a solution of soda, is removed, and the aluminium hydroxide is dissolved in dilute sulphuric acid. This solution is treated with a potassium salt to obtain alum, or is evaporated to furnish *aluminium sulphate.* The solution of soda is worked up into crystallised soda.

In the manufacture from bauxite this mineral is heated with sodium carbonate or with a mixture of Glauber salt and carbon, and the fused product levigated, sodium aluminate being obtained. Bauxite consists mainly of ferruginous aluminium hydroxide, with more or less silica.

Alum is one of the most important salts used in practice. It crystallises in colourless, transparent, sometimes very large octahedra, and is sparingly soluble in cold water, though readily soluble in hot water. The solution has a somewhat acid, astringent taste. Alum melts when heated in its own water of crystallisation, and when this is expelled forms a white spongy mass (alumen ustum), sparingly soluble in water. It decomposes on calcination.

Alum is very largely used in dye-works, in colour-making, in the tawing industry, in paper-making, &c.

Neutral or cubical alum is obtained by digesting alum with alumina, or by boiling 12 parts of alum with 1 part of slaked lime, &c. Cubical alum has the formula $K_2SO_4,Al_2S_2O_9$, and crystallises in cubes.

Sodium Alum ($Na_2SO_4,Al_2(SO_4)_3+24H_2O$; mol. w., 917)

is obtained by adding pure Glauber salt to a solution of aluminium sulphate heated to 50° to 60° C. On standing a certain time the double salt crystallises out from the solution.

Sodium Aluminate ($Al_2Na_2O_4$; mol. w., 164)

This salt is formed on boiling powdered bauxite with caustic soda, or by heating bauxite with soda in a reverberatory furnace until a sample no longer effervesces with hydrochloric acid. It absorbs, at least on the surface, a little moisture and carbonic acid from the air. The solutions, therefore, very often appear somewhat cloudy from precipitated alumina. The clear solutions, however, will remain so for some time if they are not stronger than 10° to 12° B.

Sodium aluminate is obtained in a very pure state by dissolving precipitated alumina with caustic soda. It is largely used in dye-works and calico-printing as a mordant, but is not very suitable for the manufacture of lake colours, these latter becoming dry and hard.

Aluminium Acetate ($Al_2(C_2H_3O_2)_6$; mol. w., 408)

This is obtained by precipitating a solution of aluminium sulphate with sugar of lead, barium acetate, or calcium acetate. The solution, separated from the sulphates, is used *per se* or evaporated at moderate heat. In the latter form aluminium acetate is a gelatinous, deliquescent mass. It is seldom used in colour-making.

Aluminium Chloride ($Al_2Cl_6(+12H_2O)$; mol. w., 265·8)

is formed by precipitating a solution of aluminium sulphate with barium chloride or calcium chloride. It is obtained in an anhydrous condition by heating a mixture of alumina and carbon in chlorine gas. In colour-manufacture it is used in solution only.

Alumina ($Al_2(OH)_6$; mol. w., 155·8)

Alumina is manufactured by treating sodium aluminate with milk of lime, calcium aluminate being formed:

$$Al_2(NaO)_6 + 3Ca(OH)_2 = Ca_3Al_2O_6 + 6NaOH.$$

The washed precipitate is dissolved with hydrochloric acid, and the solution again treated with calcium aluminate, whereupon alumina and calcium chloride are obtained:

$$Ca_3Al_2O_6 + 12HCl = 3CaCl_2 + Al_2Cl_6 + 6H_2O.$$
$$Al_2Cl_6 + Ca_3Al_2O_6 + 6H_2O = 2Al_2(OH)_6 + 3CaCl_2.$$

The manufacture of alumina, used in making lake colours, will be described later on with the lakes.

Alumina, under ordinary conditions, is not soluble in water, but is dissolved in considerable quantities by caustic alkalies. It acts then as an acid, and combines with the metallic oxides to form the so-called aluminates. It is insoluble in ammonia, though soluble in aluminium acetate or aluminium chloride. It is very extensively used in the manufacture of lakes, where it serves as a base (carrier).

Properties of Aluminium Salts

All soluble aluminium salts have a particularly strong astringent, sour-sweet taste, are colourless, and have an acid reaction. They part with their acid on calcination. The salts that are insoluble in water are mostly dissolved by hydrochloric or other mineral acids. Caustic alkalies give a slimy precipitate of alumina, redissolving in an excess. The same precipitate is formed by ammonia, but is not soluble in an excess of the precipitating agent. Ammonium sulphide gives a precipitate of alumina. Alumina does not combine with carbonic acid. When moistened with nitrate of cobalt and heated before the blowpipe the aluminium salts give a characteristic refractory bright blue mass. The aluminium salts show a great tendency to form double salts (alum). They are largely found combined with silica in the form of various minerals and stones, and therefore belong to the most abundant materials known (see *Earth colours*).

Tests for Aluminium Salts

Alum.—An analysis of alum is mostly confined to testing for the presence of iron and free sulphuric acid. The test for iron is performed with potassium ferrocyanide or sulphocyanide. Alum should be absolutely free from iron.

The test for free sulphuric acid consists (according to Giesecke) of adding logwood tincture, which turns slightly yellow if free acid is present, and a deep violet red when the aluminium salts are quite neutral.

The shape of the crystals and the appearance of the commercial product also afford a criterion of purity.

Aluminium sulphate must be tested for the presence of iron, free acid, Glauber salt, water, and in the case of cheaper brands for arsenic also. Iron is tested for by acidifying with nitric acid and adding potassium sulphocyanide or ferrocyanide. For free acid the logwood test is applied, as for alum. Arsenic is detected by hydrogen sulphide or by Marsh's test. Glauber salt is tested for by precipitation with ammonia. The filtrate must be evaporated, and the residue calcined, taken up with water, and tested with barium chloride. The amount of water can be calculated by drying a sample at 100° C. Commercial aluminium sulphate is rarely free from iron.

Aluminium chloride is rarely tested, except, perhaps, for the iron, as indicated above.

Aluminium Acetate.—Besides the determination of the specific gravity, it should be tested for iron compounds.

Alumina (aluminium hydroxide).—This being usually sold for colour-making purposes in a watery white paste containing 25 per cent. of dry matter, the water content must be determined. If the alumina is not perfectly washed it may contain Glauber salt or sodium carbonate with traces of ferric hydroxide. The two first-named salts can be tested for with barium chloride in the filtrate from a sample shaken up with water; iron in a nitric acid solution. Good alumina should be entirely dissolved by acetic acid. Adulterations with blanc fixe, china clay, clays, &c. remain undissolved on treating the paste with mineral acids.

b. ANTIMONY SALTS

Antimony Sulphide (Sb_2S_3; mol. w., 335)

This is the most widely known of all the native antimony ores, and is named *antimonite* (stibnite, or antimony glance). It generally forms long crystals of the rhombic system, or foliaceous masses with a characteristic metallic lustre and of a leaden or steely grey colour. It is dry and hard, fuses very easily, and volatilises when heated out of contact with the air. Antimony sulphide serves as a raw material for most antimony salts.*

Antimonious Chloride ($SbCl_3$; mol. w., 225·7)

is a white crystallised, buttery substance in the cold, melts at 72° C. to an oily mass, and boils at 230° C. It deliquesces easily in the air. Treated with a large volume of water, it is decomposed and forms a white precipitate (Algarot). This precipitate, however, does not form if the concentrated solution of antimonious chloride be treated with a solution of tartaric acid or hydrochloric acid before dilution.

Antimonious chloride is manufactured by dissolving antimonite in hydrochloric acid. After the evaporation of the water the residue is distilled. According to E. Kopp, the dissolving is considerably facilitated by a previous moderate roasting in a current of air containing steam, whereby the antimony sulphide is mostly converted into antimony oxide, while sulphurous acid escapes. Antimony oxide is very soluble in hydrochloric acid.

Tartar Emetic ($K(SbO)C_4H_4O_6 + \frac{1}{2}H_2O$; mol. w., 332·4)

This salt is largely used for dyeing purposes and to manufacture lake pigments. It crystallises in brilliant rhombic octahedra, soluble in 13 parts of cold or 3 parts of boiling water. When treated with acids it gives precipitates that are soluble in hydrochloric acid or tartaric acid. Tartar emetic is, as its name implies, an emetic, and is poisonous if taken in a large quantity. Of late it has been replaced by the cheaper akaline double salts of antimony fluoride, the most important of which is

Ammonium Antimonfluosulphate†

($SbF_3,(NH_4)_2SO_4$ with 46·94 per cent. oxide of antimony)

This compound crystallises very easily in the hexagonal system, and is the most readily soluble salt of the whole group of antimony fluoride double salts. 1 part of water dissolves at 24° C. 1·4 parts of this salt, and at boiling temperature 1 part of water will dissolve as much as 15 parts of the salt.

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* Of late antimony sulphide is largely used for colour manufacturing purposes. In France, and especially in Italy, the manufacture of antimony white, as a substitute for white lead, has made a great advance, facilitated by prohibitive laws against white lead pigments. [TRANSLATOR.]

† The lactic acid salts have lately somewhat displaced the antimony salts for the purposes mentioned. [TRANSLATOR.] See *Farben-Ztg*, xiii. 471.

c. ARSENIC COMPOUNDS

Arsenic (*Arsenious Acid* As_2O_3; mol. w., 198)

Arsenic—viz., arsenious anhydride—occurs naturally, though rarely, as so-called arsenic flowers. The artificially manufactured arsenic crystallises generally in brilliant transparent octahedra of the tesseral system, sometimes, however, in the rhombic system, and is therefore dimorphous. When heated, arsenic volatilises, without previous fusion, and forms a colourless vapour, which condenses as a sublimate on cold bodies. Finely ground, it forms a dense white, odourless, and nearly tasteless powder, rather sparingly soluble in water. It is more readily soluble in caustic alkalies or alkali carbonate, by means of which the technical arsenic solutions are made. Arsenic is readily soluble in hydrochloric acid. On heating arsenic to its volatilisation temperature for some time it becomes amorphous and fuses to a colourless, transparent glass, which, however, becomes cloudy in the air, afterwards porcelain white, and at last quite opaque—*i.e.*, reverts to the crystalline modification. The amorphous (vitreous) modification of arsenious acid has quite a different physical character from the crystalline form, it being, for instance, much more readily soluble, and in greater quantities than the crystalline arsenic—1 part of crystalline arsenic requires 335 parts of water (15° C.) for its solution, whereas 1 part of the amorphous modification needs only 108 parts at the same temperature. At boiling heat the difference is less considerable, 1 part of crystalline arsenic being dissolved by 46 parts of water, 1 part of amorphous arsenic by 30 parts of water.

Arsenious acid is one of the most violent poisons known (see "Arsenic Disease").

Arsenic is manufactured by roasting arsenic ores. It is obtained from cobalt, nickel, tin, and silver ores containing arsenic as a by-product at blue colour works (see p. 200) in the metallurgical treatment of tin, silver, &c. The ores containing arsenic are there roasted in reverberatory furnaces, and the fumes are led through flues and chambers, where they sublime to a white mass. Small quantities of antimony oxide and sulphide are sometimes found in the arsenious acid.

Arsenic is used in colour manufacture for producing emerald green and other arsenic copper colours. Commercial arsenic, if not adulterated, will contain only coke ash in small quantities as a mechanical impurity, and should therefore be entirely volatile. The sublimation is performed best in a porcelain dish, covered with another or with a cover-glass. If when the test is carefully applied, viz., at a moderate temperature, the first portion of the sublimate has a slight reddish tinge, the arsenic contains small quantities of sulphur. Selenium is revealed in commercial grades by a reddish shade. The amount of selenium can be tested for by heating the arsenic in question with a solution of potassium cyanide. This latter removes the whole of the extremely finely distributed selenium, which can then be precipitated with dilute hydrochloric acid.

The vitreous modification of arsenic, known in the trade as *white glass*, must be purer too than the crystalline arsenic, being obtained from the latter by sublimation. White glass of a reddish shade (*red arsenic glass*) is contaminated with lead or iron sulphide from the sublimation. *Yellow arsenic glass* contains free sulphur also from the sublimation.

d. BARIUM SALTS

Barium Carbonate ($BaCO_3$; mol. w., 197)

This salt occurs native as the mineral *witherite* (see *Earth colours*), crystallises in rhombic columns, and serves as a raw material in the manufacture of the barium salts. It is artificially obtained as a white, amorphous, earthy, tasteless, and inodorous powder by precipitating a soluble barium salt with sodium carbonate (see *Lake colours*). It is soluble in nitric and hydrochloric acids, and in water containing carbonic acid. Barium carbonate is poisonous.

Barium Sulphate ($BaSO_4$; mol. w., 232·7)

is found native in very considerable quantities as so-called *barytes*, heavy spar, or, as it is termed by lead-miners, cawk. It is abundantly found in Germany, and in very large quantities in Derbyshire, while in Cornwall, Devonshire, Cumberland, and some parts of Wales and Ireland it is also found and worked. Native barytes can, like witherite, serve as a raw material for the production of other barium salts, but, as explained on p. 77, is rather troublesome to work. The *artificial barium sulphate, blanc fixe,* sometimes called *permanent white,* is obtained by precipitating a soluble barium salt with sulphuric acid The various methods of manufacturing permanent white have been already described in Part I. (see p. 75). As a by-product, blanc fixe is formed in considerable quantities in the manufacture of hydrogen peroxide from the precipitation of barium peroxide with sulphuric acid. It is a white, earthy, very heavy, tasteless, inodorous powder, insoluble in water and acids, and only very sparingly soluble in dilute sulphuric acid. In consequence, all the barium salts can be tested for with dilute sulphuric acid. Conversely, soluble barium salts are used in testing for sulphuric acid.

Barium Chloride ($BaCl_2 + 2H_2O$; mol. w., 244)

This combination is of very great importance in colour manufacture, and especially in the production of lakes. It crystallises from aqueous solutions as transparent rhombic plates, readily soluble in water. It is nearly insoluble in concentrated hydrochloric or nitric acid. In the anhydrous state barium chloride forms a white mass, readily soluble in water, and fuses at a strong red heat. The aqueous solutions are of a disagreeable sharp taste, and are extremely poisonous. Crystallised barium chloride is obtained by dissolving barium carbonate or barium sulphide in hydrochloric acid (see pp. 75 and 77). It has the power of precipitating the acid coal-tar dyes from aqueous solutions, as beautiful coloured bodies, mostly quite fast to water. On this property is based the practical application of barium chloride in the manufacture of colour lakes.

Barium Sulphide (BaS; mol. w., 169)

The manufacture of this substance has been described on p. 77. It forms a grey white to greyish yellow crystalline or granular mass, which decomposes in water to barium hydroxide and barium hydrosulphide $Ba(SH)_2$: $2BaS + 2H_2O = Ba(OH)_2 + Ba(SH)_2$. The polysulphides of barium are obtained by boiling the monosulphide (BaS) with sulphur.

Tests for Barium Compounds

With aqueous or acidified solutions of barium salts, dilute sulphuric acid immediately forms a strong, dense white precipitate. When a very small quantity of barium is present this white precipitate forms slowly, and as a turbidity only. The barium salts are precipitated by solutions of gypsum (calcium sulphate). Barium chloride and barium nitrate give a yellowish green colour to the non-luminous part of the Bunsen flame.

c. LEAD COMPOUNDS

Neutral Lead Carbonate ($PbCO_3$; mol. w., 266)

This compound is found native as *cerussite*, mostly in the form of white transparent, well-defined rhombic crystals. It is artifically obtained by precipitating soluble lead salts with alkali carbonates, and forms then a dense white powder insoluble in water. It is very easily decomposed by dilute mineral acids, carbon dioxide being liberated. It is obtained in the purest state by precipitating a solution of neutral lead acetate (sugar of lead) or lead nitrate with ammonium carbonate. Neutral lead solutions also give with sodium or potassium carbonate a precipitate of lead carbonate, but the composition of the precipitate varies according to the concentration and temperature, and has not yet been exactly defined.

Basic Lead Carbonate (*White Lead*)

The manufacture and properties of white lead have been thoroughly described in the second part (see pp. 89–118).

Lead Sulphate ($PbSO_4$; mol. w., 302)

This substance occurs native as the mineral *anglesite*, and crystallises in the rhombic system. It is artificially obtained by the precipitation of a soluble lead salt with sulphuric acid or soluble sulphates, as a dense white precipitate, forming a soft white powder when dried. It is absolutely insoluble in water and dilute acids; and though, like barium sulphate, it is appreciably soluble in concentrated sulphuric acid, it separates again on dilution with water. Lead sulphate dissolves in strong nitric acid on boiling for some time. It is undecomposed by heat, though it fuses and acquires a crystalline character when recooled. At red heat, in presence of carbon, it is completely reduced to metallic lead, whilst sulphur dioxide escapes. It is also reduced to metallic lead by zinc in a solution of common salt.

Lead sulphate is chiefly used in colour manufacture in a pasty state as an addition to the lead chromates, and as a base for litho printer's lakes from coal-tar dyes. For these purposes it is obtained, as a by-product of the manufacture of aluminium acetate, from lead acetate and aluminium sulphate in the form of a paste containing variable proportions of water. It must always be thoroughly washed before use.

Lead Nitrate ($Pb(NO_3)_2$; mol. w., 330)

This salt forms large milk-white or opaque octahedral crystals, obtained by dissolving metallic lead or litharge in dilute nitric acid and evaporating the solution. It is soluble in cold water, very readily so in hot water, and serves numerous purposes in the manufacture of colours—*e.g.*, lead chromates or certain aniline lakes (vermilionettes and geranium lakes).

Neutral Lead Acetate (*Sugar of Lead*; $Pb(C_2H_3O_2)_2 + 3H_2O$; mol. w., 378) crystallises in large transparent monoclinic plates or columns, speedily efflorescing in the air. Sugar of lead is readily soluble in water, very sparingly soluble in alcohol. The solution has at first a sweet, but afterwards disgusting, metallic taste. When dissolved in the ordinary more or less hard tap water the solution is generally cloudy, and clarifies on the addition of a little acetic acid. This peculiarity is due to the lime content of the water, which precipitates very finely divided lead hydroxide, the latter being converted into lead acetate by the free acetic acid added. Sugar of lead is manufactured by dissolving metallic lead or litharge in acetic acid. The pure kinds are obtained by a repeated crystallisation. Sugar of lead is very poisonous. In the manufacture of colours it is mostly used for producing chromates (chromes, orange chrome, red chrome), the various lead carbonates, lead sulphate, &c. It also serves as a precipitating agent in the manufacture of lakes. On being heated it decomposes to lead carbonate and acetone.

Basic Lead Acetate

Sugar of lead will dissolve, further, considerable quantities of lead oxide, basic salts of variable composition being formed. They are known as mono-, di-, and tri-basic acetates. The last-named, $2Pb(C_2H_3O_2)_2 + 2PbO$, is sometimes used under the name *lead vinegar*. In general they serve the same purposes as sugar of lead (see pp. 107–109; 138; 144).

Lead Chloride ($PbCl_2$; mol. w., 277)

This compound is found native, as the mineral *cotunnite*, in the crater of Vesuvius. It is best obtained artificially by treating lead oxide with hydrochloric acid, or by precipitating a soluble lead salt with a solution of common salt, and then forms a dense crystalline white precipitate. It is sparingly soluble in cold water, but easily and completely soluble in hot water. When strongly heated the crystals melt, and when recooled, form a horny mass (sometimes called horn lead) that can be cut with a knife. Neutral lead chloride combines with lead oxide to form (probably) basic chlorides, the production and properties of which have already been described under chrome yellow (see pp. 133–135).

Lead Oxide (PbO ; mol. w., 222·4)

There are two modifications of lead oxide (see p. 258), one pale lemon, the other of a yellowish red colour. The former melts when heated to redness, and changes into the second modification. On recooling it forms a crystalline mass, volatilising at white heat. Lead oxide is moderately soluble in water, but is readily soluble in nitric or acetic acid. The yellow modification, the production of which has already been described on page 259, is the "dross," or so-called *massicot*. The reddish yellow modification, *litharge*, is formed as a by-product in the metallurgical treatment of silver and gold.

Lead Sesquioxide (Pb_2O ; mol. w., 428·8)

This oxide is a velvety black powder, which when treated with acids at 400° C., with exclusion of air, decomposes to metallic lead and lead oxide. The "browning" of the metallic lead on exposure to the air seems to be due to the formation of this sesquioxide. When heated in the air lead sesquioxide forms lead oxide (see p. 92).

Lead Peroxide (PbO_2; mol. w., 238·4)

is found native as a mineral in rhombohedral crystals, or in lumps of an iron-black colour. If prepared artificially it forms a dense, dark grey, amorphous powder, easily decomposing, when heated, to lead oxide, whilst free oxygen escapes. It is therefore a powerful oxidising agent. When treated with concentrated sulphuric acid it disengages oxygen gas; with hydrochloric acid, chlorine; the corresponding lead salts being left. Lead peroxide is decomposed by the influence of light to red lead (Pb_3O_4 or Pb_4O_5) and oxygen gas. It is best obtained by treating red lead with nitric acid (see p. 258). By precipitating a solution of sugar of lead with sodium carbonate, and afterwards with chlorine gas, lead peroxide is also obtained in a very pure state. Chlorine hereby exerts an oxidising effect on the lead oxide by the decomposition of water.

Tests for Lead Compounds

Except when changed in character by coloured acids (for instance, chromic acid), the lead salts are, without exception, colourless bodies, and only a few are soluble in water. Their solutions have an unpleasant sweet taste, redden litmus paper (acid reaction), and when treated with caustic soda or potash deposit a white precipitate of lead hydroxide, soluble in an excess of the precipitant. Hydrogen sulphide forms with acid solutions of the lead salts a dense black precipitate of lead sulphide. When treated with sulphuric acid or soluble sulphates a dense white precipitate of lead sulphate is formed, insoluble in water or dilute acids. Hydrochloric acid throws down from concentrated solutions a white precipitate of lead chloride, completely soluble in hot water. If metallic cadmium or tin is placed in solutions of the lead salts, metallic lead is deposited in a very peculiar form (the "lead tree"). Mixed with soda and heated in the reducing flame with charcoal, the lead salts form a yellow incrustation of lead oxide, beads of metallic lead being also formed by reduction. All lead compounds are poisonous, and when taken in small doses into the human body cause sometimes a peculiar disease, lead colic (see p. 116).

The analysis of the lead salts in colour works is generally limited to the determination of sugar of lead, lead sulphate, lead nitrate, red lead, and litharge.

Sugar of Lead.—When the solution is precipitated (as a qualitative test) with hydrogen sulphide the filtrate should not leave any residue on evaporation. The pure white commercial product seldom contains more than 2 per cent. of impurities. Intentional adulteration is very rare. Sometimes cheaper brands are found on the market, stained yellow or brown by the acetic acid used in their manufacture (pyroligneous acid). Even these cheap brands are free from intentional adulteration, any cheap admixed salts, like Glauber salt, common salt, &c., being easily detected. In the analysis of sugar of lead it must always be remembered that this salt is readily decomposed by the carbonic acid of the air, the liberated acetic acid volatilising and leaving a solid salt, which does not dissolve completely in hot distilled water, but deposits lead carbonate.

The water content is determined by drying at 120° C. The ordinary proportion is 14·25 per cent. (according to the formula $Pb(C_2H_3O_2)_2 3H_2O$ = 188·995). 10 grms. of anhydrous sugar of lead are dissolved in hot distilled water, and filtered through a tared filter into a 250 c.c. flask. Lead carbonate remains on the filter, and can be afterwards dried and weighed direct. 50 c.c. of the solution, 2 grms. of the salt, are diluted with water, strongly heated, and treated with an excess of oxalic acid. A white precipitate of lead oxalate is formed, which coalesces at boiling heat, and can be decomposed after sufficient washing with sulphuric acid. Lead sulphate is separated from the solution of the oxalic acid, and this latter is titrated with a standardised solution of potassium permanganate. Here Fe × 1·989 = lead oxide; × 3·382 = sugar of lead. To determine the acetic acid 50 c.c. of the solution are boiled with a weighed excess of normal sodium carbonate, the resulting lead carbonate is filtered, and the excess of the soda titrated back with normal hydrochloric acid. The rest gives anhydrous acetic acid, = 26·921 per cent. of the pure salt.

Lead Sulphate.—A sufficiently exact test for lead sulphate is to wash a large sample of the paste (25 to 50 grms.), first with dilute sulphuric acid, and afterwards with warm water, the residue being dried and weighed. A quantitative test should always be made for blanc fixe, gypsum, or clay, which may be present as an adulteration. Blanc fixe and clay are tested for by boiling the washed lead sulphate paste with soda, until it is entirely converted into lead carbonate. It is then filtered, washed, and the residue on the filter is dissolved with nitric acid. If blanc fixe and clay are present they remain undissolved. Calcium sulphate is tested for by treating the paste with hydrochloric acid (gypsum being soluble with this acid), the filtrate being tested with barium chloride.

Lead nitrate is much less used than sugar of lead in colour-making. Being sparingly soluble, it is rarely adulterated. Hence a perfectly clear solution in water is already a good sign of quality. In the case of moist goods tests must be made for the moisture content, and, if necessary, for lead.

Red Lead.—Intentional adulterations with lead oxide could be easily detected by the dull appearance of the ware; and only bright sorts should be used in colour-making. Hence it is seldom necessary to test the percentage of lead peroxide, the examination being restricted to barytes, brick dust or coal-tar dyes. The first two named are found by boiling the red lead with nitric acid and alcohol (see p. 258), red lead being readily dissolved, while the adulterations remain behind.

If on shaking red lead up with alcohol the latter becomes yellowish or reddish, or shows a more or less pronounced greenish fluorescence, the presence of coal-tar dyes is indicated. These adulterations, however, are comparatively rare.

Lead Oxide (litharge, &c.).—The oxide being readily soluble in acetic or nitric acid, any adulterations with barytes, ochres, brick dust, &c.—very seldom met with—can be easily and immediately detected.

f. BORON COMPOUNDS

Boric Acid (*Boracic Acid*; H_3BO_3; mol. w., 62)

Boric acid is found native, partly in the free state and partly in combination with alkalies. In the free state it is found in the vapours and gases of certain volcanoes and several hot springs, especially in Italy, California, the State of Nevada, and several other places. The most important sources of the acid in Italy are the *Maremma* of *Tuscany*. The hot vapours issue from fissures in the earth, especially at Monte Cerboli, M. Rotondo, Sasso, Serrazano, Lago, Castel Nuovo, &c., generally in considerable quantities. They have a very high temperature, and contain, in addition to steam and boric acid, carbonic acid, sal ammoniac, and hydrogen sulphide. The springs are called *fumaroli* or *suffioni*. To obtain the boric acid, a number of brick tanks, filled with water, are built in terraces, and as many as possible natural or artificial (bored) *fumaroli* are conducted into the tanks. The water stands for a certain time in the highest tank, from which it runs, for saturating purposes, into the next one below, the emptied tank being filled up again with water, and so on. When the water is fully saturated with boric acid it is finally run into large brick collecting basins, where the coarse admixtures gradually settle down. The clear solution is then concentrated in pans, heated by the hot vapours of the *fumaroli*, and the pure acid is obtained by repeated recrystallisation.

Crystallised boric acid forms white tabular or scaliform crystals, greasy to the touch, and with a nacreous lustre. Boric acid dissolves somewhat sparingly in cold water, but more readily in hot water, and the solutions have a peculiar bitter taste. On recooling the hot solution a copious deposition of crystals occurs. When heated, boric acid intumesces considerably, and if exposed to a temperature of 80° C. for some time parts with one molecule of water: $H_3BO_3 - H_2O = HBO_2$. It melts at 160° C. to a colourless liquid, and when heated more strongly loses a further quantity of water, and forms the anhydride: $2HBO_2 - H_2O = B_2O_3$.

This latter is a colourless, transparent glass, changing back after a certain time in the air to the hydrate by reabsorption of water.

Boric acid is used in colour manufacture for producing Guignet's green.

Borax (*Sodium Borate*; $Na_2B_4O_7 + 10H_2O$; mol. w., 382)

This is the most important salt of boric acid, and is sometimes used in colour-making. It forms colourless, transparent, more or less efflorescent, monoclinic crystals, which, when heated, intumesce considerably and part with water of crystallisation. Borax tastes slightly alkaline, and dissolves in water to an alkaline solution. The crystals melt at a high temperature to a clear glass, which soon becomes cloudy, probably by absorption of water.

It is manufactured on a large scale from the boric acid of the *suffioni*, and is found too in the water of several lakes in China, Tibet, and other Asiatic countries, whence it comes on the market as "tincal."

Boron compounds give in the reducing flame a characteristic green coloration. The quantitative determination of boric acid is very difficult, since it forms no salts that are quite insoluble in water. It must therefore be estimated by difference after all other constituents of the compound under examination have been determined.

g. CADMIUM COMPOUNDS

Cadmium Sulphate ($CdSO_4 + 4H_2O$; mol. w., 280)

is the only salt used in colour-making. The method of manufacture has already been described on p. 152. The salt forms large, hard, colourless, transparent crystals, readily soluble in water.

The cadmium compounds give with hydrogen sulphide a yellow precipitate that is insoluble in ammonium sulphide. When heated with soda on charcoal before the blowpipe they give a multicoloured incrustation. Aqueous solutions of cadmium compounds redden litmus paper. Caustic alkalies give a white precipitate, insoluble in excess of the precipitating agent. Cadmium is determined quantitatively as sulphide or oxide (by calcining the carbonate).

h. CALCIUM COMPOUNDS

Calcium Chloride ($CaCl_2 + 6H_2O$; mol. w., 219)

In the calcined (anhydrous) state calcium chloride is a white, porous, pumice-like mass, with a sharp, bitter taste. When strongly heated in the air it melts, and parts with chlorine, the resulting solution then having an alkaline reaction. Calcium chloride is very hygroscopic and readily deliquescent, and must therefore be kept in tightly closed vessels. It dissolves in water with a considerable disengagement of heat. After a careful concentration the solution deposits crystals with six molecules of water, which deliquesce very easily. These hexagonal crystals dissolve in water with absorption of heat, and when heated part with the whole of their water of crystallisation.

Calcium chloride is best obtained by dissolving calcium carbonate (chalk, marble waste, &c.) in commercial hydrochloric acid, with a brisk evolution of carbon dioxide.

$$\underbrace{CaCO_3}_{\text{Calcium carbonate}} + \underbrace{2HCl}_{\text{Hydrochloric acid}} = CaCl_2 + H_2O + CO_2.$$

To free the product from iron the completely saturated solution is treated with a thin milk of lime and thoroughly well stirred for some time, whereupon all the iron in the solution is precipitated as ferric hydroxide and ferric oxide in the form of a greyish yellow mud. The top liquor is then filtered through cloth or straw. Calcium chloride is obtained as a by-product in the manufacture of (ammonia) soda. In colour manufacture it is used as a precipitating agent for many coal-tar dyes, and in the manufacture of artificial lime carbonate.

Calcium Carbonate ($CaCO_3$; mol. w., 100)

The native calcium carbonate has been thoroughly described with the white earth colours (see "Chalk"). Calcium carbonate is obtained artificially as a soft white powder by precipitating a solution of a calcium salt with soda. It is sometimes used as a base for colour lakes. If the calcium solution is treated with soda a slimy mass is first formed, turning by-and-by into a white precipitate, which settles down to the bottom. Stirring considerably assists the formation of the precipitate.

The chemical reaction is explained by the following equation:

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$$

The precipitate is washed with pure water until all the sodium chloride is removed. In most cases this is, however, unnecessary.

Calcium Sulphate (*Gypsum;* $CaSO_4 + 2H_2O$; mol. w., 172)

Native gypsum is thoroughly described under *Earth colours*. Artificial calcium sulphate is obtained as a by-product in many factories as a fine white, light powder suitable for mixing with specifically light lead chromates.

Calcium Hypochlorite ($Ca(OCl)_2 + 4H_2O$; mol. w., 214·5)

This salt is the active agent in the bleaching powder now so largely used, which is a mixture of calcium hypochlorite, calcium chloride, and calcium hydroxide. According to Odling, its formula is $CaOCl_2$. The bleaching powder is a white, sometimes moist, easily agglomerated powder, with a slight odour of chlorine. In water it parts with the calcium hypochlorite and calcium chloride, the hydroxide being left. The aqueous extract has a slightly greenish yellow colour, and when treated with acids disengages considerable quantities of chlorine. Bleaching powder is decomposed by the weakest acids, even by carbonic acid, forming with this latter calcium carbonate and free hypochlorous acid, this latter immediately decomposing into free chlorine and oxygen. The same reaction takes place if bleaching powder is treated with soda:

$$1.\ Ca(OCl)_2 + CO_2 = CaCO_3 + 2Cl + O;$$

$$2.\ Ca(OCl)_2 + Na_2CO_3 + H_2O = CaCO_3 + 2NaOH + 2Cl + O;$$

or with dilute sulphuric acid:

$$3.\ Ca(OCl)_2 + H_2SO_4 = CaSO_4 + H_2O + 2Cl + O.$$

Still more important, however, is the treatment with hydrochloric acid, which latter also furnishes chlorine, four atoms being therefore liberated.

$$4.\ Ca(OCl)_2 + 4HCl = CaCl_2 + 2H_2O + 4Cl.$$

The oxidising effect of the liberated chlorine by one or other of the above reactions is based on the decomposition of water, whereby hydrochloric acid is formed and oxygen disengaged: $H_2O + 2Cl = 2HCl + O$. One molecule of calcium hypochlorite therefore has the same oxidising effect as two atoms of oxygen.

In the manufacture of *bleaching powder* chlorine gas is led into chambers containing a layer of lime slaked to a powder. This quickly absorbs the chlorine, heat being disengaged:

$$2Ca(OH)_2 + 4\,Cl = Ca(ClO)_2 + CaCl_2 + 2H_2O.$$

The chambers are constructed of earthenware tiles, sandstone flags, or bricks, painted over with asphaltum varnish or coal tar, asphaltum mastic being used as a vehicle. The temperature in the chambers should not exceed 50° C., otherwise potassium chlorate would be formed, a substance of no bleaching action. Bleaching powder is generally manufactured at soda works in order to utilise the hydrochloric acid obtained as a by-product. Chlorine gas is set free when manganese dioxide is treated with hydrochloric acid.

Bleaching powder is often used in colour-making as an oxidising agent, especially in the manufacture of Prussian blue.

Tests for Calcium Salts

The aqueous solutions of the calcium salts are precipitated by alkali oxalates, carbonates, and phosphates. Sulphuric acid and sulphates form a precipitate of white calcium sulphate with concentrated solutions. The calcium salts that are insoluble or nearly insoluble in water generally dissolve in hydrochloric acid or nitric acid. Calcium oxalate is insoluble in acetic or oxalic acid. Calcium salts give a reddish yellow tinge to the lower part of the Bunsen flame.

i. CHROMIUM COMPOUNDS *

Chromium Salts

Besides *potassium* and *sodium bichromates*, the preparation of which has been thoroughly described in the manufacture of the lead chromates (see p. 135), use is sometimes made in colour making of the chromium sulphate and chrome alum, which may therefore be briefly described.

Chromium Sulphate ($Cr_2(SO_4)_3 + 18H_2O$; mol. w., 718)

Chromium sulphate crystallises in blue-violet octahedra, and is obtained by dissolving chromium hydroxide in sulphuric acid. The violet aqueous solution of these crystals turns into green when heated, and furnishes on evaporation a green amorphous mass, which dissolves in water to a green solution. This on standing reverts to the violet form.

Chrome Alum (*Potassium Chromium Sulphate*; $CrK(SO_4)_2 + 12HO_2$, or analogous to Potassium Alum, $K_2Cr_2(SO_4)_4 + 24H_2O$; mol. w., 999)

On heating potassium bichromate with sulphuric acid and alcohol, the chromic acid is reduced to chromic oxide. The red-coloured liquid gradually turns green, and on prolonged standing to violet. When cold again it deposits large dark violet to black-red coloured octahedra, chrome alum. It is also formed as a by-product in the manufacture of certain coal-tar dyes; for instance, aniline violet, anthracene red, aniline green, &c., in making anthrachinone. It has the same properties as ordinary alum (potassium alum). Chrome alum dissolves in water to a violet solution, turning green when heated. The solution contains the two salts in a separated condition. After prolonged standing the violet colour returns. Chrome alum is sometimes used—but only in very small quantities—for precipitating certain coal-tar dyes in the manufacture of lakes. The chromium salts are tested for before the blowpipe by the borax bead, to which they impart a characteristic green coloration.

Quantitative Analysis of the Chromates

Sodium and Potassium Bichromates, Lead Chromate

Commercial *potassium bichromate* is, as a rule, very pure (98 to 99 per cent.). It nearly always contains a small quantity of potassium sulphate (0·5 to 1 per cent.), and a very small residue, insoluble in water (0·25 to 0·5 per cent.). It is usually guaranteed to contain 67·5 to 68 per cent. of chromic acid.

Sodium bichromate, made on the large scale, is generally less pure than the potassium salt. The content of Glauber salt is larger, and the residue, insoluble in water, is sometimes considerable, the adherent moisture being also often considerable. It is manufactured either in a finely crystallised form with two molecules of water of crystallisation or in an anhydrous state as irregular lumps with a guaranteed content of 73 to 74 per cent. of chromic acid. The chromic acid being the sole important constituent for practical purposes, the examination is generally limited to that acid if the external appearance of the sample does not afford a sufficient guarantee of purity.

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* Another element belonging to the same group of metals, *Uranium*, is now becoming a new material for colour manufacture, *i.e.*, *Uranium pitch ore*, the native Uranium compound. At Joachimsthal (Bohemia) the ores are now worked up on a large scale to Uranium colours, the most important of which, *Uranium yellow*, is used for *al fresco* painting, and also for colouring glass and china ware. [TRANSLATOR.]

Titration with Potassium Permanganate

The solution of the salt, after being acidified with sulphuric acid, is first treated with a known excess of iron ammonium sulphate. The existing ferrous sulphate is oxidised by the chromic acid to ferric sulphate, the chromic acid being thereby reduced to chromous sulphate :

$$6FeSO_4 + 2CrO_3 + 6H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 6H_2O.$$

The solution is strongly diluted with boiled water, and the quantity of ferrous sulphate left unoxidised by the chromic acid is titrated with permanganate (see analysis of lead chromate).

Complete Analysis

A weighed quantity of chromate is dissolved in water, the chromic acid reduced by boiling with hydrochloric acid and alcohol to chromium chloride, and the chromium hydroxide precipitated at boiling temperature by means of ammonia (in presence of a little ammonium sulphide). It is then filtered, washed with hot water, dried, heated to faint redness, and weighed as chromic oxide. The filtrate is evaporated first in a platinum dish, finally in a weighed platinum crucible, and the residue heated to redness to remove ammonium salts entirely. The residual potassium chloride is then weighed. If the chromate contains sulphuric acid the potassium must be weighed as sulphate. The dry mass in the platinum crucible is afterwards moistened with sulphuric acid, heated until no more sulphuric acid fumes are given off, and then calcined. The last traces of the sulphuric acid fumes are removed by the addition of very little ammonium carbonate, heating to redness once more. The addition of the salt must be repeated until two weighings give the same result.

To determine the sulphuric acid, barium sulphate and chromate are precipitated from the aqueous solutions of the salts with barium chloride, and reduced by heating with hydrochloric acid and alcohol. Barium chromate thus dissolves a chromo-chloride. The barium sulphate residue must be boiled with hydrochloric acid several times, and thoroughly well washed.*

Lead Chromate ("Chromes")

The best test for chromic acid—viz., for barytes—is potassium permanganate and ferrous-ammonium sulphate, permanganate solution being then added until the whole liquor begins to assume a pink tinge. The acid protosalts immediately decolorise the potassium permanganate, the ferrous oxide being partly converted into ferric oxide. At first the red stream of permanganate solution disappears immediately, if the liquid is shaken, but less rapidly as this addition is continued, until suddenly the whole liquid turns red, indicating complete oxidation. The solutions of the ferric salts have no reaction on permanganate. The volume of the permanganate solution left in the burette is then read off. It may be assumed that 1 grm. of ferro-ammonium sulphate requires 6·5 c.c. of permanganate solution for its complete oxidation.

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* I. Post, *Analysis*, 1888-89, vol. i.

Five grammes of the chrome yellow are now weighed out, made into a thin paste with water and concentrated hydrochloric acid, and placed in a flask of exactly the same size as used for the trial with ferro-ammonium sulphate. This flask is half filled with water, and 2 grms. of ammonium ferrous sulphate are added, and well shaken until the latter is entirely dissolved. The action of the ferrous oxide upon the chromic acid may be explained by the following equation:

$$\underbrace{2CrO_3}_{\text{Chromic acid}} + \underbrace{6FeO}_{\text{Ferrous oxide}} = \underbrace{Cr_2O_3}_{\text{Chromium oxide}} + \underbrace{3Fe_2O_3}_{\text{Ferric oxide.}}$$

The ferrous oxide therefore takes oxygen from the chromic acid, and reduces it to chromide oxide, whilst itself becoming oxidised to ferric oxide. The oxidation is revealed by the liquid in the bottom turning green. When this occurs the permanganate solution is added drop by drop to oxidise the ferrous oxide left unoxidised by the chromic acid. 4·6 c.c. of the same permanganate solution as used before may be assumed to be necessary for this purpose.

From these 4·6 c.c. of permanganate solution the quantity of ferrous oxide left unoxidised by the chromic acid can now be calculated. This quantity deducted from the 2 grms. of ferrous ammonium sulphate gives the amount of ferrous oxide necessary to convert the whole of the chromic acid into chromic oxide. Bearing in mind the previous test, in which 1 grm. of ferrous ammonium sulphate required 6·5 c.c. of permanganate solution for its complete oxidation, the quantity necessary for 4·6 c.c. can be ascertained by the following equation: $1 : 6{\cdot}5 = x : 4{\cdot}6$, wherefore $x = \frac{4{\cdot}6}{6{\cdot}5} = 0{\cdot}7077$ grm. of ferrous ammonium sulphate.

Moreover, $2 - 0{\cdot}7077 = 1{\cdot}2923$ grms. of ammonium sulphate is oxidised by the existing chromic acid. From this figure the quantity of potassium bichromate in the weighed quantity of chrome yellow can be calculated, since 1 ferrous ammonium sulphate × 0·12642 = 1 potassium bichromate; but since 1·2923 ferrous ammonium sulphate are wanted, the corresponding quantity of potassium bichromate must be $1{\cdot}2923 \times 0{\cdot}12642 = 0{\cdot}163372566$, or, shortly, 0·1634 grm. The 5 grms. of chrome yellow mixed with barytes require for their production 0·1634 grm. of potassium bichromate. It is now known that 20 grms. of potassium bichromate give exactly 44 grms. of lead chromate, from which can be calculated the quantity of bichromate necessary to give 5 grms. of pure chrome yellow (free from barytes). $20 : 44 = x : 5$, wherefrom $x = \frac{100}{44} = 2{\cdot}27$ potassium bichromate.

It was, however, found that 5 grms. of lead chromate contained only 0·1634 grm. of potassium bichromate, and from this the quantity of the pure lead chromate actually present can be calculated. $5 : 2{\cdot}27 = x : 0{\cdot}1634$, wherefore $x = \frac{0{\cdot}8170}{2{\cdot}27} = 0{\cdot}36$; viz., 5 grms. of chrome yellow (mixed with barytes) contain 0·36 grm. of pure lead chromate, or $5 : 0{\cdot}36 = 100 : x =$ per cent.

This somewhat troublesome calculation can, however, be simplified For instance, if exactly 5 grms. of the lead chromate are taken fo analysis in each case, the 0·1634 grm. of potassium bichromate need then onl be multiplied by 44 to ascertain the percentage of the pure lead chromate $0{\cdot}1634 \times 44 = 7{\cdot}18 = 7{\cdot}2$ per cent.

The data furnished by the above example are in most cases sufficien for all technical requirements.

Besides this titrimetric method, the ordinary gravimetric analysis can, o course, be employed.

k. IRON COMPOUNDS

The various iron oxides are thoroughly described under *Earth colours*, therefore the ferrous salts only need to be dealt with here.

Ferrous Sulphate (" *Green Vitriol* " ; $FeSO_4 + 7H_2O$; mol. w., 278)

This salt, mostly used in colour manufacture for producing Prussian blues, forms, in the pure state, pale bluish green crystals of the monoclinic system. The crystals effloresce easily in the air, and then become covered with a yellow powder of basic ferric sulphate, into which substance they finally decompose. When heated, ferrous sulphate, or *green vitriol*, easily loses six molecules of water of crystallisation, the seventh molecule, however, only at 300° C. Thereby the anhydrous salt is formed as a white powder. When strongly heated, ferrous sulphate decomposes to sulphur trioxide and sulphuric acid, and then to sulphur dioxide and ferric oxide. From strongly acid solutions it crystallises, like copper sulphate, in the triclinic system, and then contains five molecules of water of crystallisation ; but if crystallised from solution at a temperature of 80° C. it contains only four molecules of water of crystallisation.

Ferrous sulphate dissolves very readily in hot water, but the solutions are rarely quite clear. If these solutions stand for some time in the air a partial oxidation to ferric sulphate takes place, mostly colouring the liquid a yellowish tinge, whilst in part a basic ferric sulphate is formed as a yellow ochre precipitate. The formation of these ferric salts, however, is prevented by adding metallic iron to the vitriol solutions or by acidifying the solution with sulphuric acid.

Ferrous sulphate is very often obtained as a by-product—for instance, in the manufacture of alum. The native iron sulphide ores on standing a long time in the air are gradually leached by the rain. The solutions containing the ferrous sulphate are collected in large tanks containing scrap iron, and are thence run into the evaporating vessels, evaporated, and finally allowed to run into crystallising tanks, when crystallisation mostly takes place very quickly. In copper-mining, too (cementation process with metallic iron), ferrous sulphate is very often obtained as a by-product. It is sometimes manufactured by dissolving scrap iron in chamber sulphuric acid, or with sulphuric acid that has been used in the manufacture of nitrobenzol or for refining petroleum.

Ferrous Chloride ($FeCl_2 + 4H_2O$; mol. w., 199)

This salt forms pale green crystals, readily soluble in water to a pale green solution. It is obtained by dissolving metallic iron in hydrochloric acid, and concentrating the solution out of contact with air.

Ferrous Carbonate ($FeCO_3$; mol. w., 116)

is found native as the so-called *siderite* (iron spar). It is obtained artificially by precipitating a soluble ferrous salt with soda as a flocculent white precipitate. In the air (on drying) it absorbs oxygen and changes into ferric hydroxide, carbonic acid being liberated at the same time, a reddish brown colour being acquired.

Neutral Ferric Sulphate ($Fe_2(SO_4)_3 + 9H_2O$; mol. w., 562)

forms a yellowish white amorphous powder, readily soluble in water, furnishing a reddish yellow (in concentrated solutions a brownish red) solution. It is strongly hygroscopic and deliquescent. Dilute solutions of ferric sulphate become cloudy when heated, from the gradual deposition of basic ferric sulphate as an ochre-coloured precipitate. When the neutral ferric sulphate powder is strongly heated it decomposes, sulphur trioxide escaping and ferric oxide being left.

The manufacture of ferric sulphate has already been thoroughly described on p. 170.

Ferric Chloride (*Perchloride of Iron*; Fe_2Cl_6; mol. w., 325)

is obtained by heating metallic iron in chlorine gas, and forms small brown flakes of metallic lustre, readily fusing and subliming. The crystals deliquesce in air, and dissolve very readily in water to a reddish yellow solution. For technical purposes ferric chloride is obtained by dissolving ferric oxide in hydrochloric acid (see p. 171), the syrupy solutions depositing brownish yellow, warty, crystalline masses of the formula $Fe_2Cl_6 + 12H_2O$. The yellow solution of this latter compound decomposes on boiling, ferric hydroxide being precipitated.

Potassium Ferrocyanide (*Yellow Prussiate of Potash*; $K_4FeCy_6 + 3H_2O$; mol. w., 422)

crystallises in large, soft, pale lemon prisms, readily soluble in 4 parts of cold or 2 parts of boiling water. At 100° C. the crystals lose their water of crystallisation and become colourless. When heated out of contact with air potassium ferrocyanide is changed into potassium cyanide, nitrogen, and iron carbide, whilst on boiling with dilute acids hydrocyanic acid escapes. Heated with concentrated sulphuric acid, it furnishes nearly pure carbon monoxide. Potassium ferrocyanide is non-poisonous.

It is manufactured by calcining potash with previously carbonised materials very rich in nitrogen, such as animal residues, blood, wool dust, leather scraps, &c. The iron is introduced in the form of iron filings. The raw materials are fused together in a closed cast-iron vessel, or more often in flat cast-iron pans, forming the bed of a reverberatory furnace. The black calcination product is leached with boiling water, and the resulting crude solution is concentrated for crystallising purposes. The salt is obtained technically pure by repeated recrystallisations.

It can also be obtained from spent gas lime by treating this latter with caustic lime, calcium ferrocyanide being formed. This is decomposed by potash and potassium chloride into potassium ferrocyanide. This product is largely used in the manufacture of Prussian blue.

Potassium Ferricyanide (*Red Prussiate of Potash*; $K_6Fe_2Cy_{12}$; mol. w., 658)

This salt crystallises in anhydrous rhombic prisms of a dark red colour, and dissolves in 4 parts of water. It is formed by passing chlorine gas into yellow prussiate of potash: $2K_4FeCy_6 + Cl_2 = 2KCl + K_6Fe_2Cy_{12}$. The product is dissolved in a minimum of water, and allowed to crystallise out. It is now seldom used in colour manufacture.

Tests for Iron Salts

Ferrous Salts

In the anhydrous state these salts are white, but form pale green crystals. Their concentrated solutions are also of the same colour, and have a sweetish taste, with a strongly astringent after-taste. When strongly heated they lose their acidity if the acids are volatile, a residue of ferric oxide or ferro-ferric oxide being left. Hydrogen sulphide gives no precipitate with acid solutions. Ammonium sulphide precipitates black iron sulphide, which is readily soluble in dilute hydrochloric or sulphuric acid, with liberation of hydrogen sulphide. Potassium ferrocyanide gives a white precipitate, soon turning blue, whilst the ferricyanide produces at once a deep blue precipitate with solutions of ferrous salts.

Ferric Salts

The soluble ferric salts impart a reddish yellow colour to their solutions. They redden litmus paper, and have a sharp, astringent taste. Potassium ferrocyanide produces with their solutions a deep blue precipitate of Prussian blue. With the ferricyanide, however, no precipitate is formed, but only a darker shade of colour. Caustic alkalies and alkali carbonates give with solutions of ferric salts a precipitate of ferric hydroxide. Hydrogen sulphide reduces ferrous salts, free sulphur being formed. The neutral ferric salts are mostly colourless, but the various basic salts are red or yellow (see *Earth colours*).

Analysis of Iron Salts

Ferrous Sulphate.—If necessary at all, the analysis is limited to qualitative tests for copper and zinc. Copper is tested for by precipitating the solution (previously oxidised with nitric acid) with ammonia. In the presence of copper a blue filtrate will be obtained. Zinc is tested for by the acetate method. The filtrate is supersaturated with caustic potash, and treated with hydrogen sulphide; a white precipitate indicates the presence of zinc. If copper is present at the same time, this must be removed with hydrogen sulphide beforehand.

Ferric Sulphate.—The commercial article forms a solution of 45° to 50° B. strength, the value depending on the content of pure ferric sulphate. It always contains ferric nitrate, and not infrequently free acid. The determination of the specific gravity is generally a sufficient criterion of the technical value of the article. The content of $Fe_2(SO_4)_3$ can easily be found by Wolff's table.

Ferric Chloride.—The presence of ferrous chloride would be troublesome, and is easily detected by the blue colour of the solution obtained by addition of potassium ferricyanide. Free sulphuric acid is tested for with barium chloride. It is not necessary to test for nitric acid; but any defective solubility in water gives rise to doubt. The ferric chlorate content of the solutions can be approximately determined by Franz's table (*q.v.*).

Potassium Ferrocyanide.—It must be tested for potassium carbonate, sulphate, and chloride according to the usual methods. The quantitative analysis is best performed by treating the solution (acidified with sulphuric acid) with permanganate. The well-formed crystals and their degree of dryness are usually a reliable criterion of the quality of this salt.

l. Acetic Acid (($CH_3COOH = C_2H_4O_2$; mol. w., 60)

Pure acetic acid is colourless, boils at 118° C., and forms a crystalline mass (glacial acetic acid) at a low temperature. Acetic acid has a peculiar pungent smell, a strongly acid taste and reaction, produces blisters on the skin, and is miscible with water, alcohol, and ether in any desired proportion. The vapour is combustible. Acetic acid is a good solvent for many purposes —*e.g.*, anthracene, nitro compounds, colophony, &c. Hot acetic acid dissolves a considerable quantity of sulphur and some phosphorus. The specific gravity at 15·5° C. is = 1·056. Diluted with water, the specific gravity increases at first. Acetic acid attains the maximum density (1·075 at 15·5° C.) with 20 to 25 per cent. of water. With more water the specific gravity decreases again, so that with 49 per cent. of water it is about the same as with 2 per cent. (viz., 1·0604). The ordinary commercial acid contains 30 to 50 per cent. of water.

Commercial acetic acid is classified as follows, according to origin:

1. *Wine vinegar,* prepared from wine, and exhibiting a characteristic aromatic smell of vinegar.
2. *Fruit vinegar,* from cider or perry, contains malic acid as well as acetic acid.
3. *Spirit vinegar,* acetic acid from alcohol, a mixture of acetic acid and water.
4. *Beer, malt,* or *grain vinegar,* from unhopped beer wort.
5. *Beetroot vinegar.*
6. *Wood vinegar.*

In colour making wood vinegar is generally used, rarely that from alcohol.

Acetic acid from wood (wood vinegar).—The products obtained from the distillation of wood contain acetic acid, generally 5 to 10 per cent. of the weight of dry wood used. Various forms of apparatus are used in the distillation of wood; for instance, wrought-iron or steel retorts, 5 ft. to 30 ft. long and 3½ ft. to 7 ft. wide, connected with a condenser by an iron pipe. To collect the fluid products of distillation two different vessels are used. The more volatile oils are collected in the one at the same time with the products boiling at a higher temperature, whilst in the second—an iron or bricked vessel—the specifically heavier acetic acid is caught. The first distillates come over between 175° to 235° C., and contain very little acetic acid. They consist chiefly of water and light oils of a greenish colour. The quantity of the light oils increases with the progress of distillation, and the colour gradually changes to red. The temperature is kept at about 288° C for a certain time, and then raised to 315° C., whereupon the main bulk of the acetic acid distils over. At 400° C. the specific gravity of the oil and the acetic acid is the same, and at 450° C. the heating is stopped. About 33 per cent. of wood charcoal, 34·4 per cent. crude acetic acid, and 16 per cent. of ethereal oils are obtained, the rest being gas, which is burned. The collected acetic acid forms a dark reddish brown liquor, with smoky, acid taste, and is then purified by fractional distillation, by which the methyl alcohol is separated from the tarry compounds. After being filtered, the acetic acid is generally converted into a salt, and recovered by treating this salt with a stronger acid. The calcium salt, obtained by saturating the crude acetic acid with lime, followed by evaporation, is often used. The dry salt (sometimes called white lime) is heated to destroy the empyreumatic materials, and distilled with hydrochloric acid in a retort fitted with a copper hood and a tin condenser. Fractional distillation in a column apparatus furnishes the pure acetic acid of varying strength.

In the manufacture of acetic acid from alcohol the "quick method" is now used. The acidified alcohol is brought into intimate contact with air, at a certain temperature, to oxidise the alcohol to acetic acid in the shortest time and with a minimum of loss. This is done in large tanks (vinegar tanks), provided with a perforated double bottom. These tanks are filled to the top with curly beech shavings, acidified with vinegar. The necessary draught, furthering the rapid oxidising process, is obtained by means of suitable openings. The acidified shavings remain covered in the tanks for about twenty-four hours, being by that time thoroughly penetrated by the vinegar vapours. A wooden false bottom with many small holes is placed 8 to 10 ins. below the top of the vessel, and through these holes strings are passed projecting about an inch or so below. When the space above the false bottom is filled with alcohol these strings swell so as to fill the holes, but they also absorb and drop the alcohol, and allow it to drip on to the shavings. The space below the false bottom is ventilated by means of five to eight glass tubes. The tank is then closed with a lid, provided in the middle with a circular feed opening, through which also the air that has been deprived of its oxygen during the process can escape to the outside. During the oxidising process the temperature inside the tanks increases, so that a regular upward flow of air is caused. The charge mostly consists of a mixture of alcohol with more or less malt extract, beer or wine. The charge coming from the first tank runs into the second one, and thence, if the alcohol content does not exceed 2 to 3 per cent., to the outside as a finished product. Of late ozone too is used in this manufacture.

Acetic acid is used mostly in colour manufacture for producing acetates, especially sugar of lead, basic lead acetate, and also for the manufacture of emerald green.

Analysis.—As already mentioned, the specific gravity of acetic acid is very changeable, especially when it contains other materials, as, for instance, alcohol, methyl alcohol, acetone, &c. With regard to the tests, we may refer to the chapter on "Acidimetry." A suitable apparatus for the rapid testing of this acid is the "acetometer."

m. POTASSIUM COMPOUNDS

Potassium Hydroxide (*Caustic Potash;* KOH; mol. w., 56)

This is a white, hard, opaque body, with a crystalline fracture. It liquefies readily, deliquesces in air, and forms a solution with the water so absorbed. At the same time it absorbs carbonic acid from the atmosphere, and is gradually converted entirely into potassium carbonate. At a dull red heat caustic potash melts to a water-clear liquor of an oily consistence, and at a very high temperature it volatilises and decomposes. It dissolves very easily in water in any proportion, with considerable evolution of heat. Caustic potash has a very caustic taste, destroys all animal and most vegetable substances, attacks glass, and dissolves many minerals. It combines with acids, and then forms the corresponding salts, water being formed at the same time. In this reaction the potassium displaces the hydrogen of the acid: $KOH + HCl = KCl + H_2O$.

As the strongest saline base known, it decomposes many metallic salts by combining with the acid, whilst the metal is converted into its hydroxide: $CuSO_4 + 2KOH = Cu(OH)_2 + K_2SO_4$.

Aqueous solutions of caustic potash turn red litmus paper blue, even in the weakest solutions. Turmeric paper is coloured brown by such a solution.

Caustic potash is manufactured by treating caustic lime with potash:

$$Ca(OH)_2 + K_2CO_3 = 2KOH + CaCO_3.$$

Insoluble calcium carbonate is precipitated as a white body, the caustic potash being in solution as a water-clear liquor. The potassium carbonate is dissolved in a tenfold quantity of water, the solution heated to boiling in an iron vessel, and milk of lime is stirred well in until a sample of the water-clear filtrate treated with hydrochloric acid no longer effervesces.

The liquid in the vessel is then allowed to stand for a certain time, whereby the calcium carbonate settles quickly to the bottom. The top liquor is transferred to iron evaporating pans, and there evaporated to dryness. This residue is finally fused by strong heat, and in this state poured into moulds, where it sets to a white, opaque mass.

Potassium Carbonate (*Potash;* $K_2CO_3 + 2H_2O$; mol. w., 174)

In the pure state it forms a white, readily deliquescent mass, with a caustic taste and strongly alkaline reaction. It melts when strongly heated, without, however, being decomposed, and dissolves easily in water in any proportion.

Potash is obtained in crystals containing 20 per cent. of water (the formula being $K_2CO_3 + 2H_2O$) when hot concentrated solutions are allowed to cool.

The commercial potassium carbonate is called *potash.* It is a salt of a bluish, reddish, sometimes greenish white colour, generally contaminated by other salts, and then forms irregular moist or greasy lumps.

The oldest method of making potash is from the ashes of plants. Wood ash especially has a high content of potassium salts, potash in particular. If this ash be treated with water and the solution afterwards evaporated, a saline mass remains, the so-called *crude potash,* coloured brown by imperfectly calcined organic materials. To destroy these latter entirely the crude potash is heated in reverberatory furnaces until it turns a bluish white colour. In this state the *calcined potash* is put on the market, but still contains other salts—*e.g.,* potassium sulphate, silicate, and chloride, sodium salts, &c.

To remove the latter the calcined potash is dissolved with a minimum of water, whereby the less soluble salts partly remain behind. The clear top liquor is removed, slightly concentrated, and allowed to stand for a certain time, whereby the bulk of the extraneous salts crystallises out. On repeating the process a nearly pure potassium carbonate is obtained. Potash is also manufactured from the residues of the sugar industry and the suint from the wool-scouring process.

Far greater quantities of potash are now obtained from the Stassfurt works, especially by the *Grüneberg process* (1891), an imitation of Leblanc's soda process. The potassium sulphate is fused with lime and coal exactly as is done in the soda process; but high temperatures must be avoided. The other operations (fusing, calcination, evaporation, &c.) are also just the same.

Potash is also obtained by treating a solution of potassium chloride with magnesium carbonate and saturating with carbonic acid. The double salt of magnesium potassium bicarbonate is then heated.

The following equations explain the chemical reactions involved:

$$1.\ 2KCl + 3MgCO_3 + CO_2 + H_2O = 2MgKH(CO_3)_2.$$

$$2.\ 2MgKH(CO_3)_2 = K_2CO_3 + 2MgCO_3 + H_2O + CO_2.$$

The potassium carbonate is leached out with water; magnesium carbonate and carbonic acid are formed and used again. The method, due to *R. Engel,** is largely used in an improved form, especially in the Neu-Stassfurt salt works.

Potash is now far less used than it was at one time, being nearly entirely replaced by the much cheaper ammonia soda.

Potassium Nitrate (*Saltpetre;* KNO_3; mol. w., 101)

This salt is found native (Hungary, Spain, Persia, Egypt, and especially in India), but manufactured saltpetre is generally used.

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* F. Fischer, *Manual of Chemical Industry.*

It crystallises in the rhombic system, and forms mostly colourless, transparent, columnar crystals, sometimes hollow, which are readily soluble in water. 100 parts of water dissolve at 0° C. 13 parts of saltpetre, but as much as 247 parts at 97° C. The solubility, therefore, increases considerably with the temperature. Solution is attended with absorption of heat. When heated to 350° C. saltpetre melts to a thin fluid mass, which decomposes at a higher temperature and parts with oxygen, potassium nitrite being left as a residue. On increasing the heat still further, this too is decomposed to oxygen, nitrogen, and potassium oxide, besides very little potassium peroxide. Saltpetre, like all nitrates, is a very powerful oxidising agent. Combustible bodies, like coal, sulphur, phosphorus, iron, zinc, &c., are easily oxidised by saltpetre at a high temperature, with a bright flash and evolution of heat (gunpowder).

In the above-mentioned countries the soil, covered with the efflorescence, is leached with water, and the solution evaporated by the heat of the atmosphere. The product, the so-called *Indian crude saltpetre*, is then put on the market. The formation of saltpetre in nature is probably due to the decomposition of animal substances containing nitrogen in presence of strong alkalies, like lime, potash, &c., the ammonia formed in the process being oxidised by the atmospheric oxygen to nitric acid and water. This nitric acid combines with alkalies and alkaline earths to form nitrates.

Saltpetre is artificially obtained in the above-named manner on the so-called *saltpetre beds* by "nitrification." Animal waste products are mixed with alkaline earth, rubbish, wood ashes, &c., and piled up in heaps, which are exposed to the air for several years, and moistened from time to time with urine or the drainage of manure heaps. The heaps are provided with slight roofs to keep out the rain, and are turned from time to time to further the influence of the air. The saltpetre earth obtained in this way is then treated with water. The solutions contain saltpetre, calcium nitrate, and magnesium nitrate. To convert the two latter salts into saltpetre the solutions are treated with dissolved potash, whereby the calcium and magnesium nitrates are precipitated as insoluble carbonates, whilst saltpetre passes into solution: $Ca(NO_3)_2 + K_2CO_3 = CaCO_3 + 2KNO_3$. On evaporating the solution a crude brown saltpetre is obtained, which is purified (refined) by repeated crystallisation.

For the last forty years the major part of the saltpetre used has been manufactured by treating sodium nitrate with potassium chloride (conversion saltpetre), according to the equation $NaNO_3 + KCl = KNO_3 + NaCl$. Sodium nitrate is found native in considerable quantities, especially in Chile and Peru, while potassium chloride is obtained by mining at Stassfurt, as the so-called *kainit*. Both salts are dissolved in the molecular proportion with water and then concentrated. After a certain time sodium chloride (common salt) separates out, and saltpetre remains dissolved, being afterwards washed twice. This process rests upon the relative solubility of the saltpetre and of the common salt in the hot water; the former, as already mentioned, increases considerably with the temperature, whilst the common salt shows little change under the same conditions. The precipitated common salt can easily be freed from the adherent saltpetre, which latter is easily and completely refined. This method is also used in other countries, especially Russia.

Potassium Chlorate ($KClO_3$; mol. w., 122·5)

forms small, more or less pure white, nacreous crystals of the monoclinic system, readily soluble in hot water. The solutions have a cooling taste, like saltpetre. Potassium chlorate fuses at a slow heat without being decomposed; at higher temperatures it gives up oxygen and is converted into potassium chloride. It is a more powerful oxidising medium than saltpetre. Mixtures with coal, sulphur, antimony sulphide, and other combustible bodies explode with great force not only when heated, but also for the most part on percussion.

Potassium chlorate was formerly manufactured by introducing chlorine gas into a concentrated solution of potassium carbonate or caustic potash. At present it is manufactured by treating milk of lime at a high temperature with chlorine gas. Hereby calcium chloride and chlorate are obtained, the latter being then decomposed with potassium chloride to potassium chlorate and calcium chloride:

1. $2Ca(OH)_2 + 4Cl = Ca(OCl)_2 + CaCl_2 + 2H_2O.$
2. $3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2.$
3. $Ca(ClO_3)_2 + 2KCl = 2\ KClO_3 + CaCl_2.$

When the milk of lime is treated with chlorine calcium chloride and calcium hypochlorite, $Ca(ClO)_2$, are first formed, the latter decomposing when heated to calcium chlorate and chloride. By the simultaneous presence of chloride of potassium the above-mentioned decomposition to potassium chlorate and calcium chloride takes place. The chemical reaction can be explained in one equation as follows:

$$3Ca(OH)_2 + 6Cl + KCl = KClO_3 + 3CaCl_2 + 3H_2O.$$

Potassium chlorate is very often used as a powerful oxidising agent in the manufacture of Prussian blue. It can also be obtained by electrolysing a hot concentrated solution of potassium chloride.

Potassium Silicate (K_2SiO_3: mol. w., 154·5)

The formula K_2SiO_3 is not quite certain, no compound of potassium with silica in the crystalline state being at present known. Potassium silicate is obtained by fusing together powdered quartz, or 54 parts of pure quartz sand, 30 parts of potash, and 3 parts of powdered charcoal. The melt is afterwards dissolved with boiling water. The charcoal is added to expel the carbonic acid as carbon monoxide, since any residual carbonic acid spoils the product. Potassium silicate is found in many minerals, especially in felspar, but is not much used in colour manufacture.

Potassium Chloride (KCl; mol. w., 74·5)

crystallises in colourless, transparent cubes, and is sometimes used in the manufacture of colours. The crystals dissolve readily in water, and have a briny taste. It is obtained by treating a solution of potash with hydrochloric acid. It is found native as the mineral sylvin or kainit in large quantities in the Stassfurt mines.

Potassium Monosulphide (K_2S; mol. w., 110)

In the melted state this salt is of crystalline structure and dark red colour, deliquesces in the air, and dissolves very readily in water, heat being disengaged. When heated it forms potassium sulphate.

It crystallises from solutions after concentration as a colourless mass. It has an alkaline reaction, and is the strongest of the sulpho bases. With acids it forms hydrogen sulphide, without any deposition of sulphur. It is obtained by calcining potassium sulphate with carbon, the latter being oxidised to carbon monoxide, whilst the sulphate undergoes reduction.

$$K_2SO_4 + 4C = K_2S + 4CO.$$

If a solution of caustic potash is saturated with hydrogen sulphide *potassium hydrosulphide*, KSH, is formed.

Potassium Pentasulphide (K_2S_5; mol. w., 238·5)

This has already been dealt with on pp. 279, 280.

Testing for Potassium Salts

The lower part of the Bunsen flame is coloured violet by potassium salts, but the colour is masked by the yellow sodium flame if sodium salts are present at the same time. In this case, on viewing the flame through a cobalt glass the violet (potassium) colour shows up clearly, the sodium colour being entirely absorbed by the blue glass.

Platinum chloride gives with solutions of potassium salts a yellow precipitate of crystalline potassium platinum chloride, sparingly soluble in water and insoluble in alcohol. Perchloric acid and tartaric acid give with moderately dilute solutions of potassium salts crystalline, colourless precipitates, very sparingly soluble in water.

n. SODIUM COMPOUNDS

Caustic Soda (NaOH; mol. w., 40)

Caustic soda is very similar to caustic potash, but deliquesces still more readily in the air. From very strong solutions rhombic prisms of crystalline caustic soda, of the formula $2NaOH + 7H_2O$, melting at 6° C., separate at a low temperature. In the air caustic soda is gradually converted into sodium carbonate by absorbing carbonic acid.

Caustic soda was formerly sold as a strong solution or in a fused state, but is now sold in the solid state in sheet-iron drums. Caustic soda is sometimes made by heating strong solutions of crude soda with caustic lime (see p. 226). The solutions are concentrated in cast-iron pans to about sp. gr. 1·9, furnishing when cooled the solid commercial drum soda. Caustic soda is now obtained in soda manufacture by increasing the quantity of coal mixed with the sulphate and limestone, and leaching the crude product at once with water at 50° C. The solutions having clarified, they are quickly concentrated to sp. gr. 1·5, whereupon potassium carbonate and sulphate and common salt separate out, and the liquor acquires a brick-red colour (red solution), due to a peculiar chemical combination of iron sulphide with sodium sulphide. The solution is afterwards heated in large cast-iron pans to a very high temperature, 3 to 4 parts of sodium nitrate being gradually added for each 100 parts of caustic soda to be obtained. In proportion as the water evaporates, the saltpetre acts on the sodium sulphide and the always present sodium cyanide, a considerable quantity of ammonia and nitrogen being set free. At 300° to 360° C. the addition of saltpetre is stopped. The sulphur is now entirely converted into sulphide, a small quantity even into sulphate. Most of the sulphur must be oxidised during the subsequent fusing process by treatment with a current of air. An electrolytic method of manufacturing caustic soda has also attained a certain degree of importance. Caustic soda serves in colour manufacture for producing Bremen blue and the green copper pigments, orange chrome, and chrome red, and of late also in making the diazo colour lakes.

Sodium Carbonate (*Soda;* $Na_2CO_3 + 10H_2O$ (in the crystalline state); mol. w., 286; "*Ammonia Soda,*" *Calcined Soda, Powdered Soda;* mol. w., 106)

This most important salt is practically known in two different states—in powder and in crystals. The powdered form is mostly used in trade.

Crystallised soda forms large, colourless crystals, with 62·9 per cent. of water of crystallisation. The crystals effloresce readily in the air, and gradually turn to a white powder. This process is furthered by heating. The salt first melts in its water of crystallisation, and soon changes into the anhydrous salt, the so-called *calcined soda.* Heated to redness, it melts to a clear liquid, which when cooled crystallises again. Soda is readily soluble in water, and the solution reacts and tastes strongly alkaline. From warm solutions the salt crystallises with seven molecules of water of crystallisation.

Soda is obtained in three ways:

1. As native soda (efflorescence).
2. From the ash of plants.
3. By chemical manufacture.

Native Soda

Soda is found native as a constituent of many mineral waters, as an efflorescence from volcanic rocks, and in the water of the so-called natron lakes in Egypt, Central Africa, in the Caspian and Black Seas, India, Mexico, California, &c. On the great Hungarian plain soda is found during the summer heat as a crystalline efflorescence a crude product, which is collected and sold as such. Egyptian soda is called *tro-na,* whence comes the name natron. In Argentina native soda is found in considerable quantities, and has recently been also found in Virginia.

Soda from the Ashes of Plants

There are three commercial varieties:

1. *Soda from barilla*, cultivated on the Spanish sea-coast. The ash contains 25 to 30 per cent. of soda.
2. *Salicor*, or soda from Narbonne, with 14 per cent. of sodium carbonate.
3. *Blanquette* or soda from Aigues-Mortes, with only 3 to 8 per cent. of sodium carbonate.

The plants are collected, dried, incinerated in pits, and afterwards treated with water. The clarified solutions are evaporated.

Chemically Manufactured Soda

The manufacture of this most important salt can, of course, only be described here briefly. Until the last quarter of the past century soda was mostly manufactured by the *Leblanc process*. In this method common salt is converted by sulphuric acid (chamber acid of 52° B.) into sodium sulphate, hydrochloric acid being formed as a by-product. The sulphur is decomposed in reverberatory furnaces by a mixture of chalk and coal. In this chemical process the coal reduces the sodium sulphate to sulphide, combining with the chalk to form calcium sulphide and soda.

The *first stage* of the Leblanc process can be explained by the following equation: $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$. This operation, the production of sodium sulphate, is performed in reverberatory furnaces, provided with condensers to condense the hydrochloric acid gas. The vapours of this latter are led through a certain number of earthenware pots, connected together, and are met by a stream of water running in the opposite direction, so that the nearly saturated solution comes into contact with the most highly concentrated gas.

The *second stage*, the conversion of the sodium sulphate (generally only called "sulphate") into crude soda, is performed in reverberatory furnaces at a very high temperature (713° to 932° C.). The sulphate is intimately mixed with limestone and coal, and the mixture fused, the mass being constantly stirred with long iron crooks until blue flames of burning carbon monoxide appear. The mass is then raked into flat vessels and allowed to cool. Of late rotating furnaces are also used. The chemical process can be explained by the following equation: $Na_2SO_4 + 4C = Na_2S + 4CO$. The sulphate is therefore reduced by the coal to sulphide, the coal being oxidised to carbon monoxide.

The *third stage*, contemporary with the second one, represents the conversion of the sodium sulphide into soda by the chalk:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

In reality the process is not so easy as it seems to be from the above equation. In particular it may be assumed that the formation of a double salt, $3CaS,CaO$, calcium oxysulphide, takes place, so that part of the coal probably acts on the calcium carbonate, perhaps according to the equation $CaCO_3 + C = CaO + 2CO$. According to modern views on the reduction of the sulphate, only carbon dioxide, and no carbon monoxide, is formed: $Na_2SO_4 + 2C = Na_2S + 2CO_2$, followed by a double decomposition:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The calcium carbonate is afterwards partly reduced by the coal:

$$2CaCO_3 + 2C = 2CaO + 4CO.$$

The carbon monoxide gas, therefore, is only produced when formation of sodium carbonate is complete.

For the conversion of the crude soda into the commercial product the solutions are treated with water, this being now carried on by simple filtration in a number of sheet-iron vessels. The resulting solution contains sodium carbonate and caustic soda, besides common salt and other sodium salts in smaller quantities. The clarified solutions are concentrated, whereupon the soda separates as a white crystalline powder. This concentration is effected in special reverberatory furnaces or hemispherical pans, and the different brands are obtained by separating the products collected at various periods of the finishing process.

The Ammonia Soda Process

This procedure is of recent date. A solution of common salt is treated with ammonium bicarbonate under high pressure, sodium bicarbonate and sal ammoniac being formed: $NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$.

The sodium bicarbonate is converted, by heating, into the neutral carbonate, true soda: $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$.

This method is the one now most in use. The bicarbonate is separated from the solution by filtration, wooden filters being used, as being unattacked by the strongly alkaline solutions. The bicarbonate is then generally calcined, for which process furnaces of different kinds are used.

The only difficulty in this stage is to recover the ammonia and the carbonic acid, the loss of which must be avoided for economic reasons. The soda from the calcining furnaces is in lumps, and must therefore be powdered, generally in "Excelsior" mills.

To recover the ammonia the filtrates and washing waters containing ammonium chloride or carbonate are treated with lime, and the precipitated ammonia recovered by distillation. The recovery of the carbonic acid is generally confined to the quantities set free in the calcining process.

To manufacture *crystallised soda* (soda crystals) by boiling the bicarbonate with water, a certain amount of lime must be added to remove the last traces of bicarbonate, which would prevent the formation of good crystals and furnish only small needles. If large, hard crystals, like those obtained in the Leblanc process, are required, a certain quantity of sodium sulphate must be added to the solution, even when calcined ammonia soda is being worked. Usually 2·5 per cent. of sodium sulphate is used. Most manufacturers now also sell their crystallised soda in the form of the said needles, which is a guarantee of the absence of sodium sulphate. About 80 per cent. of the manufactured soda is made by the ammonia soda process to-day.

The electrolytic method of manufacturing soda, also from a solution of common salt, seems to have a good prospect of success.

Soda can generally be used for the same purposes as potash, and is far cheaper. On this account it is very extensively employed in colour manufacture.

Sodium Bicarbonate ($NaHCO_3$; mol. w., 84)

forms small, colourless, transparent crystals, rather sparingly soluble in water. The solution has a slightly alkaline reaction, though the salt is considered to be an acid one. By boiling it changes into neutral sodium carbonate. The same conversion is effected by heating, carbonic acid and water being set free.

In the ammonia soda process sodium bicarbonate is obtained as an intermediate product. Hence all other methods of manufacturing this salt are of only theoretical interest. It is but seldom used in colour manufacture.

Sodium Sulphate (*Glauber Salt;* $Na_2SO_4 + 10H_2O$; mol. w., 322)

Glauber salt is a constituent of many mineral waters and saline springs, and is also found in small quantities in sea-water, in animal fluids, especially in the blood, &c. Associated with gypsum, common salt, and magnesium sulphate, it forms whole mountains, as, for instance, in the valley of the Ebro, near Madrid.

The commercial product forms large, transparent crystals of the monoclinic system, with 55·76 per cent. of water of crystallisation, readily efflorescing in the air. It is also sold in the anhydrous state as "calcined Glauber salt," in the form of a fine white powder or irregular fragments. In efflorescing the crystals partly lose the water of crystallisation; when heated they melt in it, and part with it entirely at a higher temperature, the anhydrous (calcined) salt remaining behind. Glauber salt is readily soluble in water. It is most soluble at 33° C., the solubility decreasing at higher temperatures. From solutions of less than 20° C. Glauber salt crystallises with ten molecules of water; at higher temperatures the salt separates in the anhydrous state. If a solution which has been saturated at 33° C. is boiled, the anhydrous salt separates as a fine powder. Glauber salt is manufactured on a large scale with soda (see soda manufacture) by treating a solution of common salt with sulphuric acid. It is often recovered as a by-product in many chemical industries. In colour manufacture it is formed by precipitating alumina from aluminium sulphate or alum, with soda as a by-product, and is often used in the manufacture of lake pigments. Glauber salt plays an important part as a raw material in the manufacture of artificial barytes.

Sodium Nitrate (*Chile Saltpetre;* $NaNO_3$; mol. w., 85)

occurs naturally in very extensive quantities in Tarapaca and Atacama, on the frontier of Chile and Peru, as a component of a salt mixture, the so-called *caliche,* and is then called *Chile* (or *Peruvian*) *saltpetre.* It forms rhombohedra of a sometimes cubical shape, and is therefore often called *cube saltpetre*. It has about the same properties as the ordinary (potassium) saltpetre, only it is more hygroscopic, and therefore for many purposes less suitable than the more stable (potassium) saltpetre. It is of no importance to the colour manufacture, except, perhaps, as an oxidising agent in the calcining of many ferric oxide colours, and even for this purpose is rarely used now.

Sodium Nitrite ("*Nitrite*"; $NaNO_2$; mol. w., 69)

The commercial product forms small, rarely pure white or entirely transparent crystals, that are readily soluble in water and fairly stable in the air. It decomposes when heated, and with dilute sulphuric or hydrochloric acid, forms nitric acid fumes, and also nitrogen dioxide. The aqueous solutions of the pure nitrite have a neutral reaction.

Nitrite is now of considerable importance in the manufacture of colour lakes, and as it is produced direct in many colour works its manufacture will now be described.

The raw materials are generally Chile saltpetre and metallic lead, which at a temperature of about 400° C. are transformed into nitrite and lead dioxide. The chemical reaction can be explained by the following equation:

$$NaNO_3 + Pb = NaNO_2 + PbO.$$

Pure Chile saltpetre has to be used, especially free from more than a small quantity of common salt. The lead, too, must be pure, and especially free from antimony; this easily causes explosions, attended with some loss of material. The lead is applied in the form described in the white lead process (see p. 90), to facilitate the melting of the metal. 100 parts of Chile saltpetre of the best brand and 275 to 280 parts of metallic lead are generally used. The saltpetre is first melted, and the lead added in small portions to the red-hot mass. The melt is dissolved with water, the solution filtered, concentrated, and finally brought to crystallisation.

The saltpetre is melted in large, shallow cast-iron pans, set in brickwork in such a way that the flame is able to cover the whole hearth. The heated saltpetre first loses its moisture, and as the temperature rises the ever-present iodine compounds are decomposed. At about 300° C., or somewhat higher, the saltpetre becomes red hot, and at 400 to 420° C. the addition of the lead spirals can begin. The most suitable moment for this purpose having been found by a trial, *the lead is added* by degrees, one portion being allowed to oxidise completely before the next is thrown in. If too much lead were added at once the pan would burn through on the temperature being raised a little higher. To avoid this troublesome accident the whole mass in the vessel must be continually and thoroughly stirred, preferably with a mechanical device. If in this way a quite homogeneous mass is obtained, it must be scooped into cold water by means of long iron ladles, slowly and in equal portions, to avoid any spurting owing to the sudden change of temperature. The water is placed in an iron pan beside the melting-pot, so that the work can be done easily and without any loss of time. Continued stirring during the melting process facilitates rapid solution of the melt, viz., of the contained nitrite. The liquid has an alkaline reaction on account of the free caustic soda always formed in the melting process (to the extent of about 1 per cent. of the weight of nitrite obtained), and containing part of the lead oxide in solution. It consists principally of sodium nitrite and caustic soda, besides undecomposed saltpetre, common salt, and other accidentally present soluble compounds from the saltpetre. The insoluble residue consists principally of lead oxide, with varying quantities of unoxidised metallic lead and small quantities of lead peroxide. To remove the lead oxide the nitrite solution is generally treated with dilute nitric acid (7° to 8° B.) until neutral, the dissolved lead oxide being thereby precipitated as lead hydroxide, whilst the caustic soda is reconverted into saltpetre. In many works instead of nitric acid the cheaper sulphuric acid is used for neutralisation. Hereby a certain quantity of Glauber salt is formed in the solution, and separates later on during concentration (see "Glauber Salt"). After the residue has settled down the neutralised solution (density 30° to 33° B. and more) runs into tanks, and thence into iron evaporating tanks, where it is concentrated to 40° to 45° B.). After the first crystallisation the solutions are again concentrated, and the crystallisation repeated as long as a profitable crop of crystals is obtained. The last solution is evaporated to dryness, and the resulting dry product is added to a fresh charge of saltpetre, though not in large quantities, owing to the risk of contaminating the nitrite. The washed nitrite crystals from the crystallers are spread out evenly on boards, and dried at 40° to 50° C.

The insoluble residue obtained from leaching the nitrite melt with water contains considerable quantities of the partly undissolved melt and adherent nitrite solution. It is therefore treated with hot water afresh, in iron filtering vessels, provided with a perforated double bottom, covered with a strong cloth. The resulting solutions are united with the main liquor from the evaporating process or treated by themselves.

The washed lead oxide can be sold after being dried and ground or may also be worked up into red lead, sugar of lead, lead nitrite, &c. In many works it is reduced to metallic lead by roasting it with coal, which is then used for a fresh batch, but this increases the cost of the nitrite.

Nitrite can also be manufactured by calcining sodium nitrate with barium sulphide: $4NaNO_3 + BaS = BaSO_4 + 4NaNO_2$; a mixture of lime and certain lead ores being, however, generally used instead. The melt is treated as already described.*

Sodium Phosphate ($Na_2HPO_4 + 12H_2O$; mol. w., 358)

forms large, transparent, monoclinic crystals, readily efflorescing, and soluble only with great difficulty in water (8 parts salt in 100 parts water). The solution has an alkaline reaction. When heated, the crystals melt, the water of crystallisation then evaporating completely, and the salt is converted finally into pyrophosphate, $Na_4P_2O_7$.

Sodium phosphate is obtained by saturating phosphoric acid (from bones) with soda. It is sometimes used in manufacturing certain mineral colours, and also in several cases of lake pigments.

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* Nitrite is now produced on a large scale by electricity from the nitrogen of the air, and the same will soon be the case with some other nitrogen products used for colour purposes. [TRANSLATOR.]

Sodium Silicate (*Water-glass;* $Na_2Si_4O_9$; mol. w., 303·6)

has similar qualities to the corresponding potassium salt, and is found in the trade exclusively as a colourless, water-clear solution with the consistence of glycerine. Two brands are on the market—33° and 66°; *i.e.*, 100 parts contain 33 parts of dry silicate and 67 parts of water, or 60 parts of dry silicate and 34 parts of water. It is decomposed by all acids, even carbonic acid, the corresponding sodium salt being formed, whilst the free silica separates as a jelly. Sodium silicate must therefore be kept in tightly closed bottles.

Sodium silicate is obtained from 45 parts of powdered quartz, 23 parts of calcined soda, and 3 parts of carbon, or from 50 parts powdered quartz, 30 parts Glauber salt, and 8 to 10 parts carbon. At present it is nearly always obtained by dissolving diatomaceous earth with strong caustic soda under a pressure of 7 to 8 atmospheres. It is sometimes advantageously used in the manufacture of lake pigments.

Sodium Chloride (*Common Salt;* NaCl; mol. w., 58·5)

is the most important and most largely used of sodium compounds. It is found native in thick beds, together with gypsum and clay. The best-known layers are at Wieliczka, Stassfurt, in Austria, Spain, Cheshire, &c. Fairly pure natural salt is mostly ground and sold direct. It is, however, rarely obtained by mining in sufficient purity, and must generally be refined by crystallisation. The natural brine springs are very seldom saturated solutions, and for the most part have a very low content of salt. The poor brine is therefore first concentrated by evaporation in the air ("graduated"), for which purpose special plants ("graduation houses") are used. By means of pumps and pipes the brine is discharged on to a thick hedge of brushwood, through which it drips to the ground, whereby a great quantity of the water evaporates, especially in dry and warm winds. The solution concentrated in this way is collected in wooden vessels, and treated in the same way twice or three times more if necessary. When it contains about 25 per cent. of common salt it is concentrated in large iron pans, the salt then separating mostly in funnel-like crystals. The salt is then removed from the bottom of the pan with wooden shovels, filled into baskets, and dried.

Sea-water too, though it contains only about 3 per cent. of common salt, is also utilised as a source of this article, especially on the Mediterranean coast. During the summer the sea-water is run through locks into specially built basins, where it evaporates by the heat of the sun, the salt separating out in large crystals.

Common salt crystallises in cubes, sometimes forming hollow pyramids piled up like steps. It is mostly colourless, transparent, but is sometimes of a reddish, bluish, or yellowish colour. When heated the crystals decrepitate and crumble to fine powder, owing to the presence of mechanically retained water from the crystallisation process. At a very high temperature common salt volatilises. Common salt is readily soluble in water, the solubility increasing with the temperature. A certain number of chemical processes of technical importance are based upon this fact.

Tests for Sodium Salts

The sodium salts are very similar to those of potassium. Most of them dissolve in water; they crystallise easily and are colourless, if the corresponding acid is also devoid of colour. Potassium antimonate gives with moderately dilute neutral or slightly alkaline solutions a crystalline precipitate of sodium antimonate. The lower part of the Bunsen flame is coloured yellow by even the smallest quantities of sodium salts.

Analysis of Sodium and Potassium Compounds

Potash.—A bluish white colour indicates a content of potassium manganate, a reddish one ferric oxide or copper, and a grey colour is due to the presence of finely distributed carbon.

1. *The moisture content* is tested for by heating 10 grms. of the salt in a porcelain crucible until moisture no longer condenses on a superimposed glass plate, the dry substance being afterwards weighed.

2. *The insoluble constituents* are determined by dissolving 10 grms. of the potash in 500 c.c. of hot water, and filtering. The residue is washed several times on the (tared) filter, dried, and weighed with the filter.

3. *The amount of alkali carbonate* is determined with 50 c.c. of the above solutions and normal hydrochloric acid. The amount of alkali found is calculated to potassium carbonate.

4. *The chlorine content* is tested for by neutralising 50 c.c. of a solution of potash with nitric acid and titrating with $\frac{1}{10}$ N. silver solution in presence of potassium chromate.

5. *The amount of sulphuric acid* is tested for with barium chloride, 100 c.c. of the solution, after being acidified with hydrochloric acid, being precipitated in the hot state with barium chloride, and the resulting barium sulphate calculated to potassium sulphate.

6. *Potassium Content.*—50 c.c. of the solution are acidified in a 100 c.c. flask with hydrochloric acid. The sulphuric acid is precipitated with barium chloride, an excess of the latter being avoided. The flask, after being recooled, is filled to the mark and shaken, the contents filtered, and 20 c.c. of the filtrate taken to determine the potassium with platinum chloride. The weight of potassium platinochloride found is calculated to potassium carbonate.

Potassium chloride and sulphate (4 and 5) are calculated to potassium carbonate and deducted from the weight obtained in 6, the remainder being the real amount of potassium carbonate. On deducting the remainder from the weight obtained in 3 the amount of sodium carbonate is found by calculation.

Soda is generally tested for the amount of *insoluble residue*, the content of *sodium carbonate, caustic soda, sodium sulphate, common salt, iron,* and *sodium sulphite.*

50 grms. of the commercial soda are dissolved in water and allowed to stand for two to three hours, filtered, washed, and the residue dried and weighed. The filtrate and the washing waters are completed to 1000 c.c.

20 c.c. of the filtrate (equal to 1 grm. of dry soda) are treated with normal

hydrochloric acid for the test for *sodium carbonate,* and deducted from the subsequently found weight of caustic soda.

Caustic Soda.—20 c.c. of the filtrate are treated with an excess of a 10 per cent. solution of barium chloride in a 100 c.c. flask. The flask is filled with boiling water up to the mark, shaken, and tightly closed. When the precipitate has entirely settled down it is filtered through a dry filter, and the caustic soda afterwards determined in 50 c.c. of the filtrate with normal hydrochloric acid, in presence of litmus as an indicator. 1 c.c. of the acid used is equal to 0·04 grm. of caustic soda in 1 grm. of the commercial soda.

The content of sodium sulphate is tested for as follows: 20 c.c. of the filtered soda solution are acidified with hydrochloric acid, precipitated with barium chloride, filtered, washed, heated, and weighed. 1 part of barium sulphate is equal to 0·6094 part of sodium sulphate.

Common Salt.—20 c.c. of the filtered soda solution are neutralised with normal nitric acid, treated with a solution of potassium chromate until a distinct yellow colour is obtained, and then treated with $\frac{1}{10}$ normal solution of silver nitrate, until the precipitate is distinctly pink-red in colour. Each c.c. of the silver solution represents 0·00585 grm. of common salt.

Iron.—100 c.c. of the filtrate (equal to 5 grms. of dry soda) are neutralised with sulphuric acid, reduced with zinc, and treated with a $\frac{1}{20}$ normal permanganate solution. 1 c.c. of this latter = 0·0028 grm. iron = 0·056 per cent.

The test for the degree of alkalinity is best performed by dissolving 26·5 grms. of soda with water to 500 c.c. in a small flask. 50 c.c. of a solution of normal hydrochloric acid, containing 36·5 grms. of hydrochloric acid per litre, are added, litmus tincture being used as indicator. Each c.c. of normal hydrochloric acid used represents 2 per cent. of sodium carbonate.

Caustic Soda

This need only be tested for the amount of sodium carbonate present. Caustic soda being somewhat difficult to weigh, a lump is chopped off for analysis.

Assuming the lump to weigh 10·59 grms., for instance, it is dissolved in water, and the solution made up to 500 c.c. 100 c.c. of this solution are used, being then equal to 10·59 ÷ 5 = 2·118 grms. of dry caustic soda. Assume, further, that 46·9 c.c. of normal hydrochloric acid are used in the titration. These data are noted.

A further sample of 100 c.c. of the above solution of caustic soda (= 2·118 grms.) is precipitated with barium chloride on boiling, filtered hot (the funnel being covered by a glass plate), and washed with hot water until the washings no longer turn red litmus paper blue. Filtrate and washings are united, and treated with normal hydrochloric acid; 43·4 c.c. may be supposed to be necessary for this purpose. As each c.c. of the normal hydrochloric acid is equal to 0·04 grm. of caustic soda, therefore:

$$43{\cdot}4 \times 0{\cdot}04 = 1{\cdot}736 \text{ grms , or } \frac{100 \times 1{\cdot}736}{2{\cdot}118} = 81{\cdot}96 \text{ per cent. NaOH.}$$

The carbonate of soda represents 46·9 − 43·4 = 3·5 c.c. of normal hydrochloric acid =

$$3{\cdot}5 ; 0{\cdot}053 = 0{\cdot}1855, \text{ or } \frac{100 \times 0{\cdot}1855}{2{\cdot}118} = 8{\cdot}75 \text{ per cent.}$$

Sodium Nitrate (Chile Saltpetre)

The native Chile saltpetre is refined before being sent to Europe. It will therefore only be necessary to test for the amount of moisture, insoluble residue, sulphate, and chloride.

Moisture is tested for on an average sample. 10 grms. are heated in a porcelain crucible to 125° C., and weighed perfectly dry. The difference in the two weights represents the moisture.

Insoluble residues are tested for in the usual way. 10 grms. of the salt are dissolved in water, filtered, the residue washed, dried at 100° C., and weighed.

Organic bodies are determined by calcining the weighed residue, and re-weighing afterwards.

In a part of the filtrate, after acidification with hydrochloric acid, the *sodium sulphate* is tested for by precipitation with barium chloride, whilst *common salt*, if present, is tested for by titrating another part of the filtrate with $\frac{1}{10}$ normal silver solution.

Sodium Nitrite

The method of application generally requires an exact determination of the percentage of nitrite. According to A. Darbon, this is preferably done with a standardised solution (*Chem. Zg.*, xxiii., 1899, No. 17) of potassium permanganate (chameleon). If 9·1594 grms. permanganate per litre be taken, 1 c.c. of this solution represents 1 grm. of nitrite. A sample of the nitrite is weighed in a small flask, like that used in quantitative analysis, and a small quantity is then put in a funnel in the neck of a 150 to 200 c.c. Erlenmeyer flask, and dissolved in about 80 c.c. of water. Several centimetres of dilute sulphuric acid (1 H_2SO_4 to 4 H_2O) are added, and titration performed with a permanganate solution. When the colour of the permanganate begins to disappear dilute sulphuric acid is again added, this time in greater quantity, since there is no longer any risk of an escape of nitrous acid. By-and-by the red colour of the permanganate solution disappears, whereupon permanganate is added by drops, with all necessary precautions. When the red (viz., pink-red) colour is found persistent for about a quarter of an hour the titration is finished. An excess of permanganate solution would be indicated by a precipitation of manganese hydroxide. The reaction can be accelerated by heating the solution in the flask to about 30° to 40° C., but this should only be done towards the end.

o. COPPER COMPOUNDS

Copper Sulphate ($CuSO_4 + 5H_2O$; mol. w., 249·5)

is found native in considerable quantities as a secondary product of the gradual oxidation of copper ores, especially in old mines. In mines containing copper sulphide ores sulphate of copper is formed by the oxidation of these ores in the air, and slowly dissolved by the water of the mine. Copper sulphate in this case is then sometimes called *cement water*, and serves partly for the recovery of metallic copper. Old iron is then put into such cement water, and the copper separates as so-called cement copper. The greater part of this cement water is, however, worked up into copper sulphate by an evaporating and crystallising process.

Copper sulphate forms mostly large dark blue, transparent prisms of the triclinic system. The crystals effloresce easily in the air, and are then covered with a white coating. The crystals dissolve readily in water: 100 parts of cold water dissolve 40 parts, 100 parts hot water 203 parts of copper sulphate to a dark blue solution. When cautiously heated copper loses four molecules of water of crystallisation, and on being heated still further loses the fifth molecule too, and then forms a white powdery mass, gradually turning blue again in the air by absorption of moisture. Strongly heated copper sulphate decomposes entirely to sulphur dioxide and oxygen, which escape, copper oxide remaining behind:

$$CuSO_4 = CuO + SO_2 + O.$$

Copper sulphate is obtained pure when metallic copper is heated with strong sulphuric acid: $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$. This process, however, being not advantageous, dilute sulphuric acid is now generally used, being poured over coarse copper in a suitable tank provided with a double bottom, whereby, through absorption of atmospheric oxygen, copper sulphate is formed: $Cu + H_2SO_4 + O = CuSO_4 + H_2O$. By treating the so-called heated concentration stone, containing about 60 per cent. of copper, with sulphuric acid, copper sulphate is obtained on the evaporation and crystallisation of the solutions. The rest of the copper is recovered from the mother liquor by means of metallic iron. This copper sulphate contains as much as 3 per cent. of ferrous sulphate.

The so-called *Swedish copper sulphate* (the purest brand) is manufactured by the Sinding process. Cupriferous iron ores are roasted, the product treated with water, the copper precipitated as copper sulphide by the aid of hydrogen sulphide, and the copper sulphide then oxidised to copper sulphate in reverberatory furnaces.

Considerable quantities of copper sulphate are manufactured too from copper residues, copper ash, &c., being oxidised in reverberatory furnaces, and afterwards dissolved with sulphuric acid; also in the separation of gold from silver.

To free the copper sulphate from the ever-present ferrous oxide, it is dissolved in water and the solution mixed with copper nitrate, thus precipitating all the iron as an oxide, a corresponding quantity of copper oxide being dissolved at the same time.

In colour manufacture copper sulphate serves as a raw material for making Bremen blue, emerald green, and other copper pigments.

Cupric Chloride ($CuCl_2 + 2H_2O$; mol. w., 170·5)

crystallises from aqueous solutions in long rectangular prisms. The crystals lose their water when heated, and turn brown. In the anhydrous state cupric chloride forms a yellowish brown mass with a metallic taste, deliquescing in the air to a green liquor.

It is obtained by dissolving copper oxide with hydrochloric acid, or by dissolving metallic copper with aqua regia (4 parts strong hydrochloric acid (21° B.) and 1 part concentrated nitric acid).

Copper chloride is used in colour manufacture for producing certain lakes as a precipitating agent. It is obtained for this purpose by treating a solution of copper sulphate with an equivalent quantity of barium chloride :

$$CuSO_4 + BaCl_2 = CuCl_2 + BaSO_4.$$

The barium sulphate settles down, and the top liquor is then removed by syphons, filtered, and the strength of the blue-green solution ascertained from its density (see Table).

Cupric Nitrate ($Cu(NO_3)_2 + 6H_2O$; mol. w., 295·5)

This salt is sometimes used in the manufacture of lake pigments, owing to its strongly oxidising character. It forms blue columnar crystals, easily deliquesces in the air, and dissolves to a blue solution. When heated it decomposes readily, copper oxide remaining behind. It is best obtained by treating a solution of copper sulphate with lead or barium nitrate.

Qualitative Assay and Quantitative Analysis of the Copper Salts

Copper Sulphate.—An admixture of ferrous sulphate is mostly found, zinc, nickel, or arsenic being rare. The commercial articles containing more or less iron are Salzburg copper sulphate, with 76 per cent., Admont copper sulphate, with 83 per cent., and double Admont salt, with 80 per cent. of ferrous sulphate. Double sulphate is a copper sulphate crystallised together with ferrous sulphate in variable proportions.

For colour manufacturing purposes it has only to be tested for the content of iron, which is easily found by treating a solution with an excess of ammonia. Cuprous hydroxide is formed, soluble in an excess of ammonia to a bright blue liquor, while finely distributed flakes of ferric hydroxide are deposited.

In a quantitative analysis it is tested :

1. For the moisture content by heating the air-dry salt cautiously and then weighing.
2. For sulphuric acid by precipitation with barium chloride.
3. For the content of iron (zinc and nickel being absent) by precipitating as hydroxide with an excess of ammonia.

Ferrous oxide can be directly tested for by the aid of permanganate in the usual way, precipitating the copper from the same liquid with zinc (or cadmium) and hydrochloric acid.

Cupric chloride is tested merely for arsenic, the solubility in water, and the content of copper. The latter is effected by precipitating the copper with zinc and hydrochloric acid. The precipitate is then dissolved in a measured quantity of ferric chloride of known strength, and the resulting ferrous chloride is titrated with permanganate.

Cupric Nitrate.—The analysis is limited to the test for the content of iron and free nitric acid.

p. MAGNESIUM COMPOUNDS

Magnesium Oxide (*Magnesia*; MgO; mol. w., 40)

This oxide forms a fine white, voluminous, inodorous, and tasteless powder, nearly insoluble in water. It melts only at a very high temperature. Magnesium oxide is easily dissolved by most mineral acids, and their solutions yield the corresponding salts. It reacts slightly alkaline to red litmus paper. From the air it absorbs carbonic acid, and combines then to form magnesium carbonate.

It is obtained by calcining magnesium carbonate. In colour manufacture it is sometimes used as a carrier in the manufacture of very fine specifically light chrome yellows.

Magnesium Carbonate ($MgCO_3$; mol. w., 84)

is found native as a crystal, called *magnesite*, at Frankenstein (Silesia), and associated with calcium carbonate as *dolomite*, forming large masses of rock.

When a solution of magnesium sulphate is treated with soda a white, gelatinous precipitate is obtained, which, when dried, forms a soft, very light, white powder, white magnesia (magnesia alba), sometimes used as a basis in the manufacture of lakes. It is considered to be a combination of magnesium carbonate with magnesium hydroxide, of the formula $3MgCO_3 + Mg(OH)_2$.

The precipitation of this salt and its structure depend, however, largely on the concentration and the temperature of the solutions, but especially on the quantity of the precipitating medium used. If the precipitation is performed in the cold some magnesium bicarbonate remains in solution.

Magnesium Sulphate (*Epsom Salt*; $MgSO_4 + 7H_2O$; mol. w., 246·3)

forms water-clear, colourless, easily soluble, small crystals of the rhombic system. The solutions have a disagreeable, bitter taste. Heated to 150° C., it loses six molecules of water of crystallisation, the seventh molecule, however, only at 200° C. When crystallised from aqueous solutions at 30° C. it is obtained with only six molecules of water of crystallisation, and then forms crystals of the monoclinic system.

It is obtained on a large scale from bitter waters by evaporation and crystallisation. On decomposing dolomite with sulphuric acid magnesium sulphate is obtained in considerable quantities. In this case gypsum is formed, settling down to the bottom, and the magnesium sulphate liquor is then crystallised out.

The *kieserite* of the Stassfurt mines is a magnesium sulphate with one molecule of water of crystallisation. Combined with Glauber salt, it forms *astrakanite*, with 4 mol. H_2O. *Kainit* consists of magnesium sulphate and potassium chloride with 3 mol. H_2O. The two latter minerals are also found in the Stassfurt salt beds.

Magnesium Chloride ($MgCl_2 + 6H_2O$; mol. w., 203·3)

In the anhydrous state it forms a white, transparent mass. When slowly heated it melts, and forms on recooling a crystalline mass, which readily dissolves in water, the temperature rising considerably. When concentrated this solution very sparingly deposits crystals, of the formula $MgCl_2 + 6H_2O$, deliquescent, and with a sharp, bitter taste. When heated the crystals lose hydrochloric acid and water, and are converted into a mixture of magnesium oxide and magnesium chloride. Hence it is not obtainable in the anhydrous state by evaporating the solution without being decomposed. It is a constituent of many mineral waters, brine springs, sea-water, and is often found in common salt, thereby rendering it hygroscopic, pure common salt not being hygroscopical at all. In the Stassfurt mines it is found as *carnallite*, combined with potassium chloride ($KClMgCl_2 + 6H_2O$), as *tachyhydrite*, with calcium chloride, and combined with magnesium borate as *boracite* [$2(3MgO4B_2O_3) + MgCl_2$].

It is obtained dry by treating its aqueous solution with sal ammoniac and evaporating to dryness afterwards. The residue is then heated to redness, the sal ammoniac being volatilised, whilst fused magnesium chloride remains. The volatilised sal ammoniac prevents over-heating and attendant dissociation of the product.

Magnesium chloride is sometimes used in colour manufacture for producing lakes.

Tests for Magnesium Salts

The magnesium salts soluble in water have a bitter taste, and are not precipitated by ammonium sulphide, caustic soda or potash, or ammonia if ammonium salts are present. Sodium phosphate alone gives with such solutions a white precipitate of ammonium magnesium phosphate, insoluble in liquids containing ammonium salts. In very dilute solutions shaking or stirring aids the formation of the precipitate. The lower part of the Bunsen flame is not coloured by magnesium salts.

Magnesium compounds rarely need testing for colour manufacturing purposes.

q. ZINC COMPOUNDS

Zinc Sulphate ($ZnSO_4 + 7H_2O$; mol. w., 287)

occurs sometimes native as a secondary product from the oxidation of zinc ores. The artificial product generally forms large vitreous, transparent crystals of the rhombic system, readily soluble in water. From aqueous solution it crystallises easily at 30° C., but the crystals contain only 6 mol. H_2O. When heated it melts in the water of crystallisation, and loses six molecules at about 100° C., the seventh, however, only at a low red heat. When strongly heated it decomposes to zinc oxide, sulphurous acid, and oxygen. The aqueous solutions decompose, when boiled, to an insoluble basic and an acid salt.

Zinc sulphate is obtained on a large scale by dissolving metallic zinc residues with sulphuric acid or by roasting ores containing zinc. These latter are leached with hot water, the zinc sulphate crystallising on recooling. The salt is also obtained from pyrites in a similar way.

In colour manufacture it is now only used for making certain resinate lakes.

Zinc Chloride ($ZnCl_2$; mol. w., 136)

In the anhydrous state it forms a white-grey (if absolutely pure, a white), sometimes transparent mass (zinc butter), easily deliquescing and volatilising when strongly heated. It dissolves in water in any desired proportion. The aqueous solution has a repellent, burning taste, and has a strong alkaline character when concentrated. From aqueous solutions it crystallises only with difficulty as a hydrated salt. It is obtained by dissolving zinc residues with hydrochloric acid and evaporating this solution to a syrupy consistence. By decomposing pyrite residues containing zinc solutions are obtained which yield zinc chloride when treated with common salt. The Glauber salt also formed crystallises out entirely. Anhydrous zinc chloride is formed by heating a mixture of zinc sulphate with common salt, the zinc chloride being sublimed: $ZnSO_4 + 2NaCl = Na_2SO_4 + ZnCl_2$. It is used in colour manufacture as a precipitating agent for some lakes.

Zinc Sulphide (ZnS; mol. w., 97)

is found native as so-called *zinc blende*, one of the most important zinc ores, and forms bright yellow to brown, semi-transparent, regular crystals of the tesseral system.

Zinc sulphide is obtained as a white precipitate by precipitating a solution of a zinc salt with ammonium sulphide. The same product is also obtained by reducing zinc sulphate with carbon; less easily by heating zinc oxide with sulphur.

Zinc sulphide has latterly acquired special importance as a component of lithopone.

Zinc Carbonate ($ZnCO_3 + H_2O$; mol. w., 143)

It occurs naturally as so-called zinc spar, and then forms rhombohedra isomorphous with calc spar. On precipitating a soluble zinc salt with sodium carbonate a gelatinous white precipitate of basic carbonate is obtained, approximating to the formula $ZnCO_3 + Zn(OH)_2$. The precipitate is rarely used in colour manufacture.

Tests for Zinc Compounds

Most zinc combinations are soluble in water, all, however, in hydrochloric acid. The aqueous solutions redden litmus paper From the solutions ammonium sulphide precipitates white zinc sulphide; caustic potash or soda, as well as ammonia, give white zinc hydroxide, redissolved in an excess of the alkali. Alkali carbonates precipitate basic zinc carbonate. Zinc or zinc salts, when moistened with a solution of cobalt nitrate and heated in the blowpipe flame, give a bright green, unfused mass. Heated on charcoal, the zinc compounds give a yellow incrustation, turning white when cool. *The qualitative test* for colour manufacturing purposes is a very limited one, zinc sulphate and zinc chloride alone being of interest. The test, if necessary at all, is confined to the content of iron and copper, other salts, like magnesium or calcium sulphate, for instance, being innocuous.

Pure *zinc sulphate* acidified with nitric acid should not give a blue colour with yellow prussiate, nor any precipitate after an addition of sulphuric acid. In testing for calcium or magnesium the zinc must first be removed by ammonium sulphide.

The moisture content is tested for by the loss of weight on gentle heating. Sulphuric acid is tested for with barium chloride, iron by precipitation with ammonia.

Zinc Chloride—In the anhydrous commercial product only the absolute solubility with water is tested for, a proof of the absence of zinc oxychloride. The liquid salt must be tested for free acid. A strip of paper coloured with ultramarine blue (not fast to alum) and put into the solution of zinc chloride should not be decolorised in the absence of acid. The test for iron is performed as already explained for zinc sulphate. The specific gravity is a good test for the commercial article (see Table).

r. TIN COMPOUNDS

Stannous Chloride (*Tin Dichloride, Tin Salt*; $SnCl_2 + 2H_2O$; mol. w., 225)

forms small, clear, monoclinohedral prisms, readily soluble in a little water. The dilute aqueous solution decomposes, with formation of a basic salt, $Sn(OH)Cl$, producing a milk-white appearance. This circumstance arises when water containing air is used for the solution, or can be obviated by an addition of tartaric or hydrochloric acid. If the clear solution of a tin salt be exposed a certain time to the influence of the air, the tin dichloride changes by-and-by into tin tetrachloride and the above-mentioned basic salt, by absorption of atmospheric oxygen: $3SnCl_2 + H_2O + O = SnCl_4 + 2Sn(OH)Cl$. In the anhydrous state tin salt forms a white, transparent mass, melting at 250° C., and subliming at a higher temperature. Crystallised tin salt is obtained by dissolving tin filings with hydrochloric acid, evaporating and crystallising the resulting solution. According to *Noellner*,* vapours of hydrochloric acid are passed over coarse tin placed in earthenware pots, and the tin salt solution is evaporated in presence of granulated tin in tinned pans. Anhydrous tin salt is obtained by heating tin with dry hydrochloric acid vapour, or by the sublimation of the aquiferous tin salt.

It is largely used in the manufacture of lakes from natural and artificial colouring matters.

Stannic Chloride (*Tin Tetrachloride*; $SnCl_4(+5H_2O)$; mol. w., 260, water free)

is a colourless, but in thick layers yellowish, highly volatile liquid, which in air gives rise to a dense white vapour like that yielded by hydrochloric acid gas. Weak solutions, when boiled at 120° C., are resolved into hydrochloric acid gas and metastannic acid, the latter forming a bulky white precipitate:

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* F. Fischer, *Manual of Chemical Technology*, 1893.

$$SnCl_4 + 3H_2O = H_2SnO_3 + 4HCl.$$

Stannic chloride is still liquid at −20° C., and forms crystalline hydrates, with varying contents of water. It is obtained in various ways. According to *F. Fischer*,* it is prepared by dissolving tin oxide in hydrochloric acid. The stannic chloride solution is then mixed with about 10 per cent. of its weight of magnesium chloride, about 5 per cent. magnesia alba, and 20 to 40 per cent. of sand or diatomaceous earth. From the dried porous mass the tin chloride is then distilled in a current of superheated steam. It is also obtained by the distillation of a mixture of tin clippings with mercury chloride. In colour works it is generally produced by treating 80 parts of a tin salt solution (50° B.) with 48 parts of hydrochloric acid (10° B.) in a large earthenware pot with continued stirring. By-and-by 8 parts of crystallised potassium chlorate are added. The whole must be continually stirred, to prevent the liquid overflowing. With these weights a solution of tin chloride (41° B.) is obtained. The 50° B. solution is obtained by dissolving 35 parts of crystallised tin salt with 20 parts of water.

The anhydrous compound is formed when metallic tin (residues) is treated with chlorine, the tin burning and subliming to stannic chloride.

Stannic chloride is used in the manufacture of lakes, but much less than tin salt.

By dissolving tin with aqua regia the so-called "tin nitrate" is obtained, a liquid (chiefly tetrachloride) sometimes known as "composition," or physic salt. The so-called pink salt is a compound of tin tetrachloride with sal ammoniac, the formula being $SnCl_4 + 2NH_4Cl$. The highly concentrated solution of this compound is not changed on boiling, but decomposes, if heated a certain time, to a double salt, tin oxide being precipitated. The absolutely neutral reaction of the pink salt and its property of not changing at boiling heat render it more suitable in colour manufacture than the always acid tin salt.

Sodium Stannate ($Na_2SnO_3 + 3H_2O$; mol. w., 226)

forms hexagonal crystals with three molecules H_2O, and is readily soluble in water. In colour manufacture it is used like the other tin salts.

It can be obtained by fusing tinstone with caustic soda and afterwards crystallising the solution; or by treating litharge with caustic soda at 35° C. The mixture must be diluted with water, and then granulated tin added to the hot solution, sodium stannate being formed and the lead separated in the form of lead sponge. Sodium stannate gradually decomposes in the air to stannous oxide, tin, and stannic oxide, the stannous oxide also gradually oxidising to the stannic condition.

Tests for Tin Compounds

Tin Salt.—The commercial article may contain compounds of lead, zinc, and copper, and is sometimes intentionally adulterated with magnesium sulphate. If a clear solution of tin salt is treated with ammonium sulphide, the sulphides of tin, copper, zinc, and lead are obtained. The tin sulphide remains dissolved in an excess of ammonium sulphide, whilst the other sulphides are insoluble. In the test for magnesium sulphate, tin, lead, copper, and zinc must be removed by hydrogen sulphide and ammonium sulphide, and followed with sodium phosphate. The property of pure tin salt to dissolve entirely in alcohol is also utilised for analytical purposes. In the alcoholic solution of tin dichloride the zinc and magnesium sulphate remain behind as a crystalline mass, whilst stannic compounds are observable as a flocculent or powdery precipitate.

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* F. Fischer, *Manual of Chemical Technology*, 1893.

The total content of tin can be tested for by precipitating the tin with hydrogen sulphide. The tin sulphide is dissolved with nitric acid, evaporated, the residue heated and weighed as stannic oxide.

Stannic chloride is sold as a 60° B. solution, and then generally contains a certain quantity of nitric acid. It is also sold as a deliquescent mass, or—though very seldom—as large crystals with a variable content of common salt (up to 30 per cent.).

The content of nitric acid is tested for by putting a crystal of ferrous sulphate into the tin chloride solution, a bright red coloration being formed if nitric acid is present. The total content of tin is tested for in the same way as for tin salt. The specific gravity test is generally quite sufficient for colour manufacturing purposes.

Pink Salt (Ammonium tin chloride).—With regard to the very variable content of ammonium chloride, the test for the content of tin chloride is specially important. It is effected gravimetrically by a method similar to that described above.

s. ACIDS

Sulphuric Acid (H_2SO_4; mol. w., 98)

This acid being the most important for colour manufacturing purposes, its properties may be thoroughly explained.

In a very concentrated state sulphuric acid forms a thick, liquid, oily, absolutely colourless mass of sp. gr. 1·8384 (66° B.). The trade article generally appears more or less brownish in colour by accidental impurities, such as fragments of coal, dust, &c. Sulphuric acid has a rapid destructive action on organic materials (animal as well as vegetable), and must therefore always be treated very cautiously. A special property of sulphuric acid is its considerable capacity for absorbing water, which it takes up from the air, and is thereby gradually weakened. In the same proportion as the atmospheric water is absorbed, the capacity for further absorption of water decreases, until it ceases completely. The commercial acid is therefore never pure, since it always contains more or less water. This circumstance must be taken into consideration in using the acid, as the variable shades of colour sometimes obtained when sulphuric acid has been used (Prussian blue, zinc chrome, chromes, &c.) are generally caused by its readily altered strength.

Sulphuric acid can be distilled, the boiling-point, however, being very high (338° C.). During distillation it is partly decomposed, sulphuric anhydride escaping, while 98·7 per cent. of acid distils over. Below 0° C. sulphuric acid sets, and then often forms regular hexagonal prisms. If commercial sulphuric acid, which generally contains some water, is cooled below 0°, crystals of the pure acid are produced, melting at + 15° C. The molten acid remains liquid below 0°, but sets suddenly if some crystallised acid is added and then the temperature rises to + 10·5°. Sulphuric acid mixes with water in any proportion, with liberation of heat. If strong sulphuric acid is mixed with water the liquid may suddenly rise to boiling heat, and be spirted about, especially if no care is taken to secure equal distribution by thoroughly stirring (see p. 19). Another peculiarity can also be observed in the dilution. The volume of such mixtures is always less than the sum of the volumes of their components, a contraction taking place of about 29 : 1000; *i e.*, 50 c.c. sulphuric acid and 50 c.c. water at 15·5° C. will give 97·1 c.c. and not 100 c.c. of dilute acid after the mixture has been cooled to the same temperature. This circumstance allows one to assume that sulphuric acid when mixed with water not only forms mechanical mixtures, but a real chemical compound with a distinct quantity of water, the resulting heat being then explained. If, for instance, acid and water are mixed in proportion to their molecular weights, viz., 98 parts of sulphuric acid and 18 parts of water, an acid of a specific gravity 1·78 and crystallising at 4° C. is formed. This supposed chemical combination must be a very light one—for instance, like that of the combined water in crystals. When such an acid with a higher proportion of water is heated it parts with its water first, and only very little of the acid, the boiling temperature, however, increasing at the same time, until the residue in the retort shows a concentration of 98·5 per cent. Only when this point is reached does the rest distil at a constant temperature of 338°. This means that the boiling-point of such a mixture decreases proportionally to the quantity of water, and the specific gravity of the dilute acid also decreases. From the specific gravity of dilute sulphuric acid the content of pure acid can be gauged (see Table).

Sulphuric acid being one of the strongest acids, reddens blue litmus paper very distinctly even if very highly diluted (1 to 1000). By reason of its high boiling temperature, sulphuric acid displaces most other acids from their combinations, and is therefore often used in their manufacture. Sulphuric acid seems to be entirely decomposed by strong galvanic action. Hydrogen gas reduces sulphuric acid to hydrogen sulphide.

The destructive action of sulphuric acid upon organic combinations must be explained by its hygroscopic capacity—namely, that it extracts the water in the form of the component hydrogen and oxygen, the carbon then for the most part being separated or carbon combinations of a more or less black-brown colour being formed. This may explain the blackening of wood, &c, on contact with sulphuric acid, as also the brown shade of the sulphuric acid when accidentally contaminated with organic bodies.

Manufacture of Sulphuric Acid

There are three brands of sulphuric acid practically known :

1. *Ordinary sulphuric acid,* sometimes called *English acid.*
2. *Fuming sulphuric acid* (Nordhauser acid, oleum).
3. *Sulphuric anhydride* (pyrosulphuric acid).

The ordinary sulphuric acid is now manufactured on the largest scale by burning pyrites and subsequent oxidation of the resulting sulphurous acid in so-called leaden chambers. The manufacture belongs to a wider sphere of chemical industry, and can only be briefly mentioned here.

According to *G. Lunge*, sulphuric acid is produced in two stages: the formation principally depends upon an intermediate production of nitrosyl-sulphuric acid decomposed by an excess of water into sulphuric acid; the chemical reaction may be explained as follows:

$$2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2,OH,ONO;$$

and afterwards, with an excess of water:

$$2SO_2,OH,ONO + H_2O = 2H_2SO_4 + N_2O_3;$$

this latter again forming nitrous acid with water, the whole cycle beginning anew.

The oxidation of the sulphurous acid to sulphuric acid is done in spacious rooms about 15 ft. high, 100 ft. in length, and up to 35 ft. wide. The walls are of lead, and very firmly welded. These so-called leaden chambers, generally three side by side, are on a strong wooden frame, provided with a cover, and with gangways all round the chambers. The cover and the side walls of the chambers only are lead, the bottom dipping like open bells into shallow basins. At the end of the chamber plant is placed a high chimney to set up the necessary draught. Sulphurous acid and steam are introduced into the chambers, together with atmospheric air and nitric acid. The sulphurous acid is now mostly obtained by roasting iron or copper ores in special furnaces. These latter allow the draught to be regulated exactly, so that a suitable excess of oxygen can be maintained. The nitric acid is led in as such, or obtained by decomposing sodium nitrate with sulphuric acid in pans heated by the furnaces used for roasting.

The chambers are connected with two towers, one of them, the so-called *Glover tower*, being used for concentrating the sulphur dioxide gas by cooling and saturating it with nitric acid. The second, or *Gay-Lussac tower*, serves to recover the gaseous nitrogen compounds coming from the chambers. This is done by passing the gas through a mass of coke moistened with sulphuric acid. The nitrogen compounds are absorbed, and leave the tower as sulphuric acid containing nitric acid, the so-called *nitrose*. This nitrose is mixed with nitric acid and passed through the Glover tower, where it is denitrated by the sulphuric acid and discharged as pure sulphuric acid. The denitration of the nitrose is, as already mentioned, for the purpose of returning the nitrose combinations to the cycle of the chamber process.

The sulphuric acid formed in the chambers settles to the bottom. It has the specific gravity 1·55, and contains no more than 64 per cent. of pure H_2SO_4. The so-called *chamber acid* is passed into a system of leaden pans, in which it is concentrated to the specific gravity 1·75, containing then 77 per cent. of pure acid. A stronger acid corrodes the metal, so that further concentration is effected in glass or platinum vessels, generally to a specific gravity of about 1·84 (66° B.) - *i.e.*, to the specific gravity of the ordinary commercial acid.

For the manufacture of chemically pure sulphuric acid this acid must be distilled in retorts of glass or platinum.

The *fuming or Nordhauser sulphuric acid* is considered to be a solution of the anhydride, SO_3, in sulphuric acid, and is manufactured by heating ferrous sulphate, $FeSO_4 + 7H_2O$. When moderately heated it loses first its water of crystallisation, and at a higher temperature decomposes by absorption of oxygen to ferric sulphate, and this in turn to ferric oxide, sulphuric acid, and sulphuric anhydride. This latter is dissolved by the distilled acid. The heating is done in earthenware retorts, placed in rows in a furnace. The ferric oxide remaining in the retorts is known in the trade as *caput mortuum* or *colcothar*. The fuming sulphuric acid is therefore not a special chemical combination, but only sulphuric acid containing a greater or smaller quantity of dissolved anhydride. It is put on the market as a yellowish to brown coloured oily liquor of sp. gr. 1·86 to 1·9; it fumes in the air, violently absorbs the atmospherical moisture, and hisses when mixed with water. It is but very little used at present.

Pyrosulphuric acid, $H_2S_2O_7$, is now purchasable. It is made from a solution of one molecule of sulphuric anhydride in one molecule of sulphuric acid:

$$SO_3 + H_2SO_4 = H_2S_2O_7.$$

According to *Winkler's contact method*, sulphuric acid, when heated, is decomposed to sulphurous acid, oxygen, and water. The latter is first retained by concentrated sulphuric acid, and the mixture of sulphuric acid and oxygen is led over glowing asbestos, whereby it is converted into anhydride: $SO_2 + O = SO_3$. This Winkler process is thought likely to cause a revolution in sulphuric acid manufacture.

The true sulphuric anhydride, SO_3, forms at the ordinary temperature a colourless liquid, setting below 16° C. to a mass of felted acicular crystals like asbestos, and boils at 46° to 47° C. The commercial anhydride, sold in tin boxes weighing 130 lbs. each, contains 98 per cent of anhydride and 2 per cent. of sulphuric acid. Sulphuric anhydride acts as a poison and corrosive on the organism.

Nitric Acid (HNO_3; mol. w., 63)

Nitric acid forms a colourless, fuming liquor, with an acid smell and a specific gravity of 1·52. It sets at $-50°$ C., boils at 80° C., absorbs water from the air, and turns yellow in the sunlight, with partial decomposition to nitrous acid, water, and oxygen. Nitric acid stains the skin, wool, silk, and feathers yellow, dissolves many metals, and easily cedes part of its oxygen to substances like phosphorus, sulphur, &c., which are thereby oxidised. Nitric acid mixes with water in any proportion, with reduction of its specific gravity. The acid of sp. gr. 1·42 is considered to be a special combination of nitric acid with water, of the formula $3H_2O,2HNO_3$. This combination has a steady boiling-point, and is not changed by boiling or in sunlight. If highly dilute nitric acid is distilled, pure water is given off first, and the boiling-point constantly increases, but remains steady at 123° C., whereupon an acid of sp. gr. 1·42 distils over.

Organic bodies are attacked by strong as well as by dilute acid. Certain organic colouring matters are decolorised—for instance, indigo solution.

This also proves the strongly oxidising action of nitric acid. Organic bodies are decomposed in such a way that a portion of the hydrogen is eliminated as water, and is replaced by the atomic group NO_2, formed by the partial decomposition of the nitric acid. Such organic bodies are called *nitro compounds*, and will be described later on in the manufacture of lakes. When organic bodies are treated with nitric acid the temperature rises; sometimes a flame is observed; and therefore the so-called "nitrification" must always be done in the cold (in vessels packed with ice).

Nitric acid behaves in a peculiar manner towards solutions of ferrous sulphate. If nitrates or free nitric acid are mixed with strong sulphuric acid, and afterwards a strong solution of ferrous sulphate is added, so that the liquids do not mix together, but form separate layers, a coloured zone can be observed, reddish, violet to black-brown, according to the quantity of nitric acid, at the place of contact between the two liquids. This peculiarity is used as a qualitative test for nitric acid or its salts.

Red fuming nitric acid is a dark red, opaque liquor, giving off thick red vapours in the air, and is considered to be a saturated solution of nitrogen tetroxide, N_2O_4, in nitric acid. It is largely used as a powerful oxidising agent.

Manufacture of Nitric Acid

Nitric acid is manufactured on the large scale by decomposing Chile saltpetre with sulphuric acid: $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$, or at a higher temperature: $2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$.

Horizontal cast-iron cylinders are now used for this purpose, built into a furnace so as to be equally bathed by the hot gases. In the front end is placed an opening for supplying the Chile saltpetre through an earthenware funnel. During the process this opening is closed by an earthenware plate. The back of the apparatus has an iron pipe, luted with clay, for leading the nitric acid vapours into a system of clay pots. These pots (sometimes called tourills or bombonnes) are connected together by coils or elbow-pipes, and the last one is connected with a tower (the absorption tower), fitted inside with a considerable number of horizontal earthenware plates, kept moist with water running down as a very thin stream. The water gradually flows through from one pot to another, condensing the nitric acid vapours, so that the pot nearest to the furnace therefore contains the strongest nitric acid. These pots can be emptied from time to time by hydraulic pressure. The nitric acid obtained in this way is generally yellow or red from nitrogen tetroxide, and must be *bleached*—*i.e.*, the acid is heated in earthenware pots or coils until no more red fumes of nitrous acid escape; or hot air is passed in until decoloration occurs. At present air is supplied under pressure to the distilling vapours. The hydrochloric acid, always present, is then volatilised as chlorine gas.

Red fuming nitric acid is obtained by treating one molecule of sulphuric acid with two molecules of Chile saltpetre. On heating the mixture colourless nitric acid is first received, as long as any free sulphuric acid is present. When the reaction is finished a mixture of sodium bisulphate and saltpetre (two molecules) remains in the cylinder. This residue is strongly heated, and then gives neutral sodium sulphate and nitric acid, the latter, however, at once decomposing to nitrous acid, oxygen, and water.

The red fumes of the nitrous acid dissolve in the distilled nitric acid, and then form the red fuming nitric acid.

Hydrochloric Acid (*Muriatic Acid*; HCl; mol. w., 36·5)

Commercial hydrochloric acid represents a solution of hydrogen chloride gas in water, and is in the pure state a colourless, fuming liquid, with a sharp smell and very acid taste. It very strongly attacks most metals and dissolves them. Crude commercial hydrochloric acid is generally more or less yellow from ferric chloride, and contains besides small quantities of sodium sulphate, common salt, selenium, and arsenic. The solution, if saturated in the cold, has the specific gravity 1·21, and when heated a large volume of hydrochloric acid gas escapes. In practice an acid of about 21° B. (sp. gr. 1·17) or even less (sp. gr. 1·152 = 19° B.) is generally manufactured. When heated the boiling-point increases to 110° C., remaining steady at this point. By distillation at this temperature an acid with a sp. gr. of only 1·10 is obtained, containing 20·2 parts of hydrochloric acid gas in 100 parts, and is considered to be a combination of one molecule of hydrogen with eight molecules of water: $HCl + 8H_2O$. This acid no longer fumes in the air.

The pure combination of chlorine with hydrogen, hydrogen chloride, is a colourless gas, and gives off thick white, sharply smelling, irrespirable fumes in the air. It acts very injuriously upon the respiratory organism, easily producing inflammations on the skin. It reddens blue litmus paper very strongly, and is very easily soluble in water. One volume of water dissolves at 0° C. nearly 400 volumes of hydrochloric acid gas. This great solubility in water explains the formation of the white vapours in the air. This latter always containing water vapour, the hydrochloric acid gas combines with it to a less volatile combination, forming the fog aforesaid. In absolutely dry air hydrochloric acid gas gives no fumes at all.

The aqueous hydrochloric acid is obtained as a by-product in the manufacture of soda from common salt (see page 315). On distilling the crude hydrochloric acid (free from arsenic) the chemically pure acid is obtained. Nowadays hydrochloric acid is also obtained from electrolytically manufactured chlorine gas, being passed with steam over coal heated to dull redness, a very pure product being obtained. The method of manufacturing hydrochloric acid from common salt is, of course, only practicable if worked as a by-process of the Leblanc soda process.

Oxalic Acid ($H_2C_2O_4 + 2H_2O$; mol. w, 126)

Oxalic acid crystallises in colourless, transparent, small monoclinic prisms with 2 mol. H_2O, which escape when it is heated at 100° C. The crystals effloresce after a certain time in the air, and then form a powder. Oxalic acid dissolves in 9 parts of cold water, and more readily in warm water. The solution has a strongly acid taste, and is very poisonous.

Oxalic acid is a component of many plants, and is to day exclusively manufactured by melting wood shavings or sawdust with caustic potash. The product is treated with water, the solution boiled with milk of lime, and the resulting calcium oxalate is decomposed by sulphuric acid. The solution, which also contains sulphuric acid and gypsum, is then concentrated to 15° C., and a certain time afterwards the gypsum separates out. This latter being removed, the solution is evaporated to 30° B., the oxalic acid then crystallising on cooling. The crude acid is refined by repeated crystallisations.

Tannic Acid ($C_{14}H_{10}O_9$; mol. w., 322)

forms an amorphous, nearly colourless to slightly brown mass, of a very low specific gravity, readily soluble in water, but sparingly so in ether. Its chemical nature is not yet exactly defined. The aqueous solutions have an astringent, but not bitter taste, redden litmus paper, and easily grow mouldy in the air. Tannic acid has only faintly acid qualities. The solution treated with ferric salts gives a fine blue-black precipitate (ink), and forms insoluble compounds with tartar emetic, sugar of lead, egg albumen, and especially with gelatine. Tannic acid is precipitated from its solution by common salt and many other salts. It forms with most of the basic coal-tar dyes precipitates more or less fast to water, and it is therefore largely used in the manufacture of lakes.

Tannic acid is a constituent of sumach and gall-nuts. The powdered gall-nuts are first diffused, and then treated with ether containing alcohol, the filtered solution being afterwards somewhat diluted with water. The tannic acid is dissolved, and the impurities mostly remain in the ether. From the aqueous solution the tannic acid can be refined by precipitation with common salt, or as a distillation residue from an ether-alcohol solution. It is often called water-alcohol, or ether-tannic acid, according to the solvent used.

Tests for Acids

In colour manufacture really pure acids are rarely used, and in most cases any admixtures or adulterations of the technical acids are of no importance.

1. *Sulphuric Acid*

Test for Lead.—The metal can only be present as a sulphate. The acid is diluted (if concentrated) with the same volume of water and two volumes of alcohol, and is allowed to stand for a certain time. A white cloud is first obtained, gradually forming a precipitate of lead sulphate. The precipitate can be collected on a filter, washed with dilute alcohol, heated in a porcelain crucible, and the residue weighed. 1 grm. $PbSO_4$ = 0·68317 grm. Pb.

Test for Iron.—A drop of nitric acid is added to the sulphuric acid, boiled, diluted with a little water, allowed to cool, and then treated with a solution of potassium sulphocyanide. A red coloration shows that iron is present.

Tests for Arsenic.—The acid is diluted with an equal volume of water, and then sulphurous acid gas is led in for a certain time. The excess of sulphurous acid is removed with carbonic acid, and the arsenic is precipitated with hydrogen sulphide.

The test for a small *content of nitrogen acids* is performed with a solution of diphenylamine. For this purpose diphenylamine is dissolved in a hundredfold quantity of chemically pure sulphuric acid, and cautiously added to the sulphuric acid under examination. The smallest traces of nitrogen acids are shown by a bright blue colour at the place of separation between the sulphuric acid and the diphenylamine.

2. *Nitric Acid*

Test for Chlorine.—It is neutralised with chlorine-free soda, and a few drops of silver nitrate are added. A white precipitate indicates chlorine.

Test for Sulphuric Acid.—It is almost completely neutralised with soda, and precipitated with barium chloride.

Test for Iron.—It is supersaturated by boiling with a solution of ammonia. After being filtered, washed, and heated, the flocculent precipitate of ferric hydroxide is weighed as ferric oxide, Fe_2O_3.

3. *Hydrochloric Acid*

The test for sulphuric acid (after having neutralised most of the hydrochloric acid) is performed with barium chloride. *Free chlorine* is tested for by starch and potassium iodide, *ferric chloride* with ammonium sulphide, *arsenic* by Marsh's test, or by the addition of a tin salt solution, which gives a voluminous brown precipitate.

THE LABORATORY—SUPERVISION—ANALYSIS

An efficient colour manufactory nowadays must have a well-equipped laboratory, provided with the necessary apparatus and resources for rendering a quick control and an effective management of the work possible. The laboratory should also enable the necessary trials of any one product to be made previous to its actual manufacture. The number of the colours now sold becoming year by year more considerable, especially owing to the continued progress of the coal-tar colour industry, it is quite impossible to give immediately an exact formula for all the many hundreds of pigments, or even to keep them in stock as standard types. Therefore the samples received from customers must generally first be made on a small trial scale, and afterwards manufactured in bulk. This sometimes very troublesome and protracted task may be a very expensive one if the necessary resources are not available in the works. Careful management, therefore, is incompatible with cheeseparing in laboratory expenses.

The constant necessity for comparing colour shades, standard types, and freshly manufactured shades requires, first of all, a good and steady light. The windows should therefore be on the north side, since the more they front to the south the longer will the sun enter the room direct and prevent the proper matching of the shades in question. Furthermore, besides the absolutely necessary appliances, steam-heating services should be provided, as well as a filtering, pressing, and drying plant. In a large laboratory a small motor (electric, hydraulic, or compressed air) is very useful for driving small apparatus for stirring dry mixtures or solutions. An exposure cupboard should be arranged in a place exposed to the light, or this device may be replaced by the so-called Uviol lamp (Schott glass works, Jena). This lamp (the name Uviol is a contraction of ultra-violet) furnishes highly actinic ultra-violet rays, which soon decompose colours that are not fast to light.

The trials on a small scale must be made under conditions resembling the operations in the works. This is especially the case with the right disposition of the vessels for use, the quantities of water, the duration of time, the composition and the washing and drying of the colours. All this can easily be done, and considerably facilitates the subsequent manufacture. Laboratory colours are preferably dried in the drying-rooms used for the same colours when manufactured in the works. When preparing pigments that need stirring for a certain time, this labour must be performed in precisely the same way as it is done in the works, by aid of the mechanical apparatus. Laboratory colours must also be washed in the same way as those made in the works.

It is, of course, a matter of importance to make written notes about all the trials and tests made in the laboratory. These notes contain not only simple indications about the weights used, but also remarks on the quantities of water, the temperature, &c., and chiefly all observations of any importance to the manufacturing process later on. The greatest care is necessary in this connection, since it is only by keeping a very careful record of experiments that errors can be avoided, instead of trusting to the memory.

Before a sample can be matched, to avoid trouble and loss of time the colour must be carefully analysed. A systematic analysis of the lakes from natural and artificial colouring matters has not yet been devised, but the components of the mineral colours are mostly detected by simple means in qualitative analysis. It would exceed the object of this manual to give an exhaustive qualitative analysis; therefore special books dealing with inorganic analysis should be referred to. In the following pages, however, some advice may be given with regard to the behaviour of the usual colours (excluding the colour lakes which are noticed elsewhere) toward the most important reagents, as also direct conclusions on the nature of the pigments in question.

TABLE OF THE PRINCIPAL MINERAL COLOURS.

CHEMICAL COMPOUND AND PRINCIPAL REACTIONS.

Signs: P., precipitate; E., evolution; C., carbon; w.C., with carbon; S., solution; s. soluble; Co., colour; R., residue; Surpl., excess; Fl., flame; h., heating; D., discolours.

	Hydrochloric acid.	Nitric acid.	Caustic soda.	Ammonia.	Behaviour on heating.
		A.—WHITE COLOURS.			
1. *White lead* . . . . . 2 $PbCO_3$, $Pb(OH)_2$	Hot s, CO_2 - E; cold P of $PbCl_2$	s. CO_2 - E.	s.	—	w.C.: yellow, metallic lead
2. *Zinc white* . . . . . . ZnO	s.	s.	s.	s.	Yellow; when cold, white
3. *Lithopone* . . . . . . $BaSO_4$ + xZnS	Partly s. H_2S - E.	Partly s. H_2S - E.	—	—	*id.*
4. *Blanc fixe*, $BaSO_4$ . . . . (Barytes)	—	—	—	—	w.C.: BaS; moistened with hydrochloric acid: H_2S
5. *Chalk* . . . . $CaCO_3$	s. CO_2 - E.	s. CO_2 - E.	—	—	White: CaO; with water alkaline reaction
6. *Gypsum* . . . . . . $CaSO_4$	Somewhat s.	Somewhat s.	—	—	w.C., CaS
		B.—YELLOW COLOURS.			
1. *Chrome yellow* (do. orange) . $PbCrO_4$ (do. red)	Green S., white P., s. with much water	D.	Orange	Yellow S. with white R.	Red-brown heating product; w.C.: metallic lead
2. *Zinc chrome* . . . . . 3 $(ZnCrO_4)$, $K_2Cr_2O_7$ + xZnO	Easily s., yellow Co.	Easily s., yellow Co.	Yellow Co. with white R., s. in surpl.	Yellow Co. with white R., s. in surpl.	Brown heating (or glowing) product, decomposing
3. *Barium yellow* . . . . . $BaCrO_4$	s. with sulphuric acid, white P.	s.	—	—	Green colour in the lower part of the Bunsen flame
4. ***Naples yellow***	Orange, later white	s. White P.	Orange	—	White vapours, w.C.: antimony

5. ***Cadmium yellow*** CdS	Hot s., with E. of hydrogen sulphide; S. colourless				
6. *Cassel yellow* ($PbCl_2$, 7 PbO)	s. yellow, afterwards colourless	s. white; P.; $PbCl_2$	s.	—	White, w.C.: lead
7. *Arsenic yellow* As_2S_3	—	—	s. with acid Yellow P.	Partly s.	White fume, garlic odour
		C.—BLUE COLOURS.			
1. *Bremen blue* $Cu(OH)_2 + xCuCO_3$	Green S., slight E. of carbonic acid	s.	On heating, black	s. blue	Black, lower part of the Bunsen flame green
2. *Prussian blue* Fe_7Cy_{18}	Greenish yellow, with much water blue again	Heated grey, afterwards colourless	Discolouring Brown R.	s. with oxalic acid	Red-brown: Fe_2O_3
3. *Smalt*	Boiling s., yellow Co.	—	—	—	No change
4. *Ultramarine*	Discol., E. of hydrogen sulphide	As with hydrochloric acid	—	—	No change
		D.—GREEN COLOURS.			
1. *Verdigris* $Cu(C_2H_3O_2)_2$. 2 H_2O	s. yellowish green	s. blue	When heated, black	s. blue	Colours the flame green. R. black; from acid solution iron precipitates metallic copper
2. ***Mountain green***, *Bremen green*. *Brunswick green*, &c.	s. yellowish green, often white P.	*id.*	*id.*	*id.*	
3. *Emerald green* $CuAsO_3$, $Cu(C_2H_3O_2)_2$	s. yellow green	s.	bluish, heated red yellow	Entirely s., deep blue	Black glowing product, fume with garlic odour
4. *Scheele's green* $CuAsO_3 + xCu(OH)_2$					
5. *Guignet's green* $Cr_2O(OH)_4$	s. ultimately green	—	—	—	From green to brown into black
6. *Ultramarine green*	Discol., E. hydrogen sulphide	As with hydrochloric acid	—	—	No change at first, then blue to brown
7. ***Chrome green***	R. light blue, s.	On heating discolour	Yellow	—	Brown R., w.C.: lead

TABLE OF THE PRINCIPAL MINERAL COLOURS—*continued.*

	Hydrochloric acid.	Nitric acid.	Caustic soda.	Ammonia.	Behaviour on heating.
D.—GREEN COLOURS—*continued.*					
8. *Zinc green*	Yellow s., blue R.	Yellow S., grey, bluish R.	Yellow S., yellow R.	Yellowish S., blue-violet R.	Dirty brown R.
9. *Rinmann's green* $CoOZnO$	—	green s.	—	—	—
10. *Manganese green* $BaMnO_4$	s.	s.	—	—	—
E.—VIOLET COLOURS.					
Ultramarine violet	Discol., E. of hydrogen sulphide	As with hydrochloric acid	—	—	Blue
F.—RED COLOURS.					
1. *Red lead* Pb_3O_4	White, E. of chlorine	Partly s., brown R., s. with alcohol	—	—	Yellow, w.C.: lead
2. *Chrome red* $PbCrO_4$ $P(OH)_2$	Green S., white P.	Yellow	Yellowish s., white R.	—	Red-brown glowing product, with C.: lead
3. *Vermilion*, HgS	—	—	Yellow	—	Volatile, E. of sulphur dioxide
4. *Red oxide*, Fe_2O_3	Yellow s.	Yellow S.	—	—	Deep brown; when cold: red
5. *Antimony vermilion* $Sb_6S_6O_3$	s., R. yellow, sulphide of antimony	—	Decomposed	Decomposed	White fume; w.C.: antimony
G.—BLACK COLOURS.					
1. *Bone black*	Dissolve phosphate of lime	Dissolve phosphate of lime	—	—	White
2. *Lamp black*	—	—	—	—	Burns without residue

Some Remarks on Volumetric Analysis *

To ascertain the quantity of an element or of a chemical compound two different methods are available, the gravimetric and the volumetric. In the first method the material in question is entirely precipitated from its solution by suitable reagents, added in excess, and weighed. Silver, for instance, is precipitated as silver chloride by a solution of common salt, filtered, dried, weighed, and the content of silver calculated. In the second method the same result is obtained, a suitable reagent being added in the exact quantity required, and the weight of the material in question is calculated therefrom.

The reagent is used as a standardised solution, and the volume consumed is measured. It is necessary, therefore, to control the end of the reaction by means of a change in the colour or by the formation or disappearance of a precipitate. An example will explain the principle of this method.

As is known, 108 parts of silver combine with 35·5 parts of chlorine (see p. 6), in accordance with their molecular weights. If 1000 c.c. of a liquid contain 108 parts of silver (dissolved in nitric acid), and 1000 c.c. or another liquid 35·5 parts of chlorine (as common salt), the whole quantity of chlorine combines with the whole quantity of silver to form silver chloride when these liquids are mixed, and the clear top liquor, after being thoroughly shaken, will then contain no silver or chlorine. The same will be the case when both liquids are mixed according to volume. For instance, 50 c.c. of the chlorine and 50 c.c. of the silver solution always exactly precipitate one another. From this fact it follows that if a certain quantity of the chlorine solution—*e.g.*, $\frac{1}{100}$ = 10 c.c.—is added to the silver solution, the silver of the precipitate must be $\frac{1}{100} \times 108 = 1{\cdot}08$, or, on an addition of x c.c., $= 1{\cdot}08 \times x$. If, therefore, a solution with an unknown content of silver be treated with the above mentioned solution of common salt, so long as a precipitate still forms, the quantity of the dissolved silver can be calculated from the quantity of the solution consumed.

This method of testing is quickly done, and gives exact results. It is therefore specially advisable for use in manufactories, and is the one generally practised.

The solutions used in this method are called *normal solutions*, if they contain the combining weight of the reagent in grams per litre. Solutions of only one-tenth of such combining weights are called $\frac{1}{10}$ *(deci-) normal solutions* or $\frac{1}{10}$ *solutions*. The total number of grams of the reagent per litre is called the *titre* of the solution. Some solutions being unstable, cannot be kept in stock to a constant titre; the latter, therefore, must be found by trial before use. To observe distinctly the moment of complete neutralisation recourse is had to the colour reaction of certain organic colouring matters with acid or alkaline solutions. Litmus, for instance, in an alkaline solution is blue, with an acid solution red in colour; phenolphtalein is of a red colour with an alkaline solution, colourless with an acid solution; methyl orange, a red colouring matter, is turned yellow by alkalies, red by acids. Such colouring matters are called *indicators*.

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Alkalimetry and Acidimetry

These operations serve the purpose of the test for the contents of soda, potash, caustic potash, ammonia, and acids, and are based on the property of the alkalies to form with strong acids (nitric acid, hydrochloric acid, sulphuric acid, oxalic acid, &c.) salts which do not change litmus tincture, though the latter is coloured red by the smallest quantity of free acid and blue by the smallest quantity of free alkali. If litmus reddened by acid is treated with a dilute solution of caustic soda, a moment arrives when the red-coloured liquid suddenly turns blue again. The strength and the quantity of the sodium solution necessary to the saturation of the acid being known, the amount of the acid can be calculated, the acid and the base in this case being mutually saturated in the proportion of their equivalents (see pp. 8 and 9). From the equation $NaOH + HNO_3 = NaNO_3 + H_2O$ it follows that 40 parts of caustic soda combine with 63 parts of nitric acid to form a neutral compound. To obtain a normal solution of these bodies the above-named quantity has to be dissolved and made up to a litre. Both compounds, however, are unobtainable in a suitably pure state. Oxalic acid is the only acid obtainable in crystals of a quite distinct composition. These crystals in a freshly prepared state have the formula $H_2C_2O_4 + 2H_2O$ and the molecular weight 126. Oxalic acid, however, is a dibasic acid, and therefore an oxalic acid solution of $\frac{1}{2}(H_2C_2O_4 + 2H_2O)$ would be equal to the above-named normal soda solution—*i.e.*, one containing 63 grms. per litre. By another rule the normal solution is made with half the atomic weight on dibasic and one-third on tribasic elements. Such a normal or half-normal solution is easily prepared. 63 grms. fresh crystallised, dry oxalic acid are dissolved in water, and the solution filled up to 1 litre. From this solution the normal solution is made as follows: A solution of caustic soda, free from carbonic acid, is diluted with about threefold the quantity of water. To 10 c.c. of this solution a few drops of litmus tincture are added, and then oxalic acid until the liquid just turns red. If for this purpose 25·2 c.c. are used, these and the 10 c.c. of the caustic soda solution contain equivalent quantities of reacting substances. To obtain, therefore, a solution of caustic soda equal to the normal acid, 10 c.c. must be filled to 25·2 c.c., or 396·8 c.c. to 1000 c.c.—viz., 396·8 c.c. of the above-named caustic soda solution are measured, and water added until the whole becomes 1000 c.c. The resulting solution is a normal caustic soda solution neutralising the acid solution volume for volume.

In the test for alkalies a weighed quantity of the dry substance in question is dissolved in a little water, litmus tincture is added, and afterwards the acid until the blue colour just changes red. The total number of c.c. used, multiplied by the combining weight of the alkali, and divided by 1000, is the weight of the alkalies contained in the used quantity. The figure of the abbreviated calculation, the "factor," is for caustic potash $KOH = 0·056$, for caustic soda $NaOH = 0·04$.

The conversion from red into blue being more easily observed than that from blue into red, the operation may be performed as follows: The weighed quantity of alkali is treated with an excess of normal acid, the litmus tincture therefore being distinctly red. The normal caustic soda is then carefully added until the colour just changes from red into blue. The volume of caustic soda solution used has to be deducted from the volume of the acid used, and the alkali can be calculated from the remainder. This method, the so-called "remainder method," can also be used in the test for alkali carbonates. In this case carbonic acid escapes on the addition of the normal acid, changing the litmus tincture, and therefore marking the end of the reaction. Soda and potash are therefore "standardised" with an excess of normal acid, and the carbonic acid removed by boiling. When cool again, the added excess of the normal acid is then again titrated with the normal caustic soda solution. In the test for soda and potash 1 to 5 grms. are used; to test for the alkali content of their ashes 5 to 10 grms. are taken. The troublesome boiling, whereby loss of material sometimes occurs, can be avoided if methyl orange is used as an indicator, since carbonic acid has no influence on this colouring matter.

Example.—5 grms. of soda to be tested for the content of alkali are dissolved in water. 40 c.c. of the normal acid are added, and the solution boiled until no more carbonic acid escapes. Litmus tincture is then added, and the excess of acid titrated with normal caustic soda solution:

Applied normal acid . . .	40·0 c.c.
Normal caustic soda . . .	4·9 ,,
Difference	35·1 c.c.

Therefore the 5 grms. of soda contain $\frac{35\cdot1 \times 0\cdot106}{2} = 1\cdot860$ grms., or 37·2 per cent. sodium carbonate, Na_2CO_3 free from water. The formula $Na_2CO_3 + 10H_2O$ corresponds to 37·07 per cent. of carbonate free from water. Hence the soda in question can be considered pure.

To test the ammonia content of the commercial ammonia 2 c.c. are taken, supersaturated with normal acid, and the excess titrated with litmus as indicator by means of normal caustic soda solution. To find the percentage of ammonia by weight the specific gravity is determined; *e.g.*, if the specific gravity of the liquid be 0·9100, the absolute weight of the 2 c.c. would be $2 \times 0\cdot91 = 1\cdot82$ grms.

In the same way the percentage of the various acids, nitric acid, sulphuric acid, acetic acid, &c., is determined by means of normal caustic soda solution. This test is called acidimetry, the alkaline solution being assumed to be known, and the effect of the acid substance having to be calculated. The calculation is done on the basis of the equation representing the process of neutralisation:

$$NaOH + HNO_3 = NaNO_3 + H_2O;$$

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O, \text{ \&c.}$$

As the various Tables (see at the end) giving the ratios between the contents and the specific gravity (volume weight) of the acids and their aqueous solutions, in colour manufacturing it is very often quite sufficient to state the specific gravity. In this case care must be taken by a qualitative test that the acid in question is possibly free from other dissolved substances. The specific gravity is found by the specific gravity instrument or by weighing equal volumes of acid and water. For this purpose, for instance, a small 100 c.c. flask, bearing a mark, is filled with the acid in question exactly to the mark, and then weighed. Assuming the 100 c.c. to weigh 132 grms. after the tare has been deducted, the specific gravity of the acid is then $\frac{132}{100 \text{ c.c.}} = 1{\cdot}32$, and if the acid in question is sulphuric acid the content of pure acid is then, according to the Table given, 41·5 per cent.

B.—THE NATURAL MINERAL COLOURS (EARTH COLOURS)

PART I

I.—NATURAL MINERAL COLOURS IN GENERAL-OCCURRENCE, ESTIMATION, AND EXAMINATION OF THE CRUDE COLOURED EARTHS—ADVANTAGEOUS DISPOSITION OF MINERAL COLOUR WORKS PLANT

The definition of natural mineral colours has already been elucidated in the Introduction (pp. 4 and 5), and in accordance with that definition we include under this designation all those pigments derived from those characteristically coloured minerals occurring in a ready-formed state in the earth, usually as the result of purely mechanical actions. Owing to their origin, such colours are commercially known as "natural mineral colours" (earth colours), a description which is not quite free from objection, because, strictly speaking, it should be confined to minerals which retain their character of natural coloured earths both in the crude and finished products, and have not been chemically changed during manufacture, which change is generally due to calcination or burning.

This condition would restrict the term to those materials which, from their natural constitution, can be converted without special difficulty into a fine powder fit for use as colours by the ordinary levigation or grinding processes alone. But as the natural mineral colours so largely preponderate over those prepared by calcination, it is convenient to apply the term earth colours to the whole group.

The raw materials suitable for mineral colours may occur in nature in two distinct conditions—viz., amorphous or more or less soft earths and clays, and crystalline or stony (sometimes very hard) masses. Furthermore, the natural condition of the raw materials determines the subsequent method of preparation, and also the necessity for using more or less tedious manufacturing processes and costly apparatus and machines. The value of the coloured earths depends, therefore, not only on the extent of the deposit found, but also in no inconsiderable measure on the condition of the raw materials themselves. Generally speaking, the object of the preparation of the natural raw materials is confined to converting them into a very fine powder possessing all the properties which consumers expect in a good colour. First of all these qualities is softness of texture, to which should be added good covering power, and finally a certain degree of brightness, whilst other qualities, such as fastness to light and air, are in most cases essential.

The examination of the raw materials obtained for the purpose of colour making need only extend to the determination of the three first-named points, the result indicating the method of preparation to be adopted. In judging the utility and paying character of the raw materials the following method may be preferably employed. The first important point is to secure such a sample as will ensure a reliable estimate being made of the yield obtainable from the raw material. Since very large quantities of greatly varying purity have always to be dealt with in practice, serious complications might ensue if the sample examined were taken solely from a very pure batch or portion of the raw material. Larger samples are therefore drawn from various parts of the deposit or from the heaped material, and these samples are mixed well together in a clean place either by shovelling or in some other manner, a superficial crushing of the lumps and fragments being very advisable if the nature of the material permits. The resulting mixture is spread out as a uniform layer, which is divided into four or five parts of equal size, from each of which a number of smaller samples are taken, these being again mixed together, and the operation repeated one or several times in the manner described above. The sample thus obtained may be regarded as a fairly reliable average sample.

If the crude product is of a crystalline nature it is advisable to take a large number of pieces of various kinds and to crush them, preferably in an edge-runner mill. The pulverised material is mixed at the same time to such an extent that an average sample can be drawn from the mass. When the crystalline minerals under examination are intended for the production of white mineral colours, such as barytes, gypsum, &c., the crystals before being pulverised must be freed from earthy impurities by careful washing, followed by drying. The first determination made with the average sample is the moisture content. From 100 to 200 grms. are weighed out from a large quantity of the raw material, and allowed to become quite dry in the drying-room or in the open air. The loss in weight gives the content of moisture. As, apart from the natural moisture always present, these raw products are stored in the open air without shelter and exposed to the moisture of the atmosphere (rain, snow, dew, &c.), the determination of the water content is of great importance for *valuation* purposes, especially in the case of earthy and clayey raw materials. For this reason it should never be omitted, not even when after a certain lapse of time a given raw material is obtained from the same layer as a previous batch.

The next test of the moist or dry average sample relates to the determination of the percentage of serviceable pigmentary matter. For this purpose the raw material is in nearly all cases subjected to systematic levigation, especially when it is of an earthy or clayey nature ; and it is only when the mineral is either very hard or contains very small proportions of sand, small stones, &c., that a mere sifting of the previously weighed and triturated, air-dry substance through a fine silk or wire sieve is considered sufficient. The separation of the finer pigmentary ingredients from the impurities present in the crude earth takes place as follows: Three to four numbered glass beakers of equal size, according to the kind of the raw material, are placed in a row, glass vessels being preferable, as the behaviour of the sediment and suspended matter can be more conveniently examined than in opaque vessels. The first beaker is filled three-quarters full of water, and a weighed quantity of the raw material in question is distributed therein by stirring it round with a small stick. In the case of earthy and bituminous materials this distribution, as a rule, takes place very quickly, but more slowly with clayey materials, the mass having first to be softened. After a certain interval the parts remaining suspended in the water are poured into the second beaker, and the coarse sediment in the first beaker, containing all the impurities and a certain quantity of usable colour, is stirred up again for a long time with a quantity of water equal to that poured off. The liquid found in the second beaker is left to stand. To facilitate the detachment of particles firmly adhering to the impurities the stirring in the first glass must be continued much longer than the first time; but finally even this liquid too is left to settle. If in the meanwhile a noticeable sediment has been formed in Glass II., the residual liquid is poured into Glass III., that from I. being transferred to the residue in II., whilst the residue in I. is treated with a fresh quantity of water. The same procedure is now repeated. The contents of Glass I. are again stirred, but for a longer time than before, and Glasses I. and II. are left to settle. After the lapse of a certain time, the duration of which depends on the nature of the materials under treatment, the contents of Glass III. are poured into Glass IV., those of Glass II. into Glass III., and those of Glass I. into Glass II., care being taken in decanting that no parts of the sediment escape from any of the vessels. This manipulation, repeated at gradually increasing intervals, is continued until the residue in the first beaker no longer parts with any colouring ingredients, but leaves the water perfectly clear. This condition being attained, Beaker I. is put aside without removing the residue, and the contents of the second beaker are now dealt with in exactly the same manner.

The material in the second glass, however, being already in a considerably finer state of division, the levigation process proceeds much more slowly, especially as, in order to avoid the use of unduly large quantities of water, the contents of the fourth glass (which contains the purest colour) must always be allowed to settle completely before the supernatant water is poured off. When the residue in Glass II. ceases to give up any more fine parts to the water, the operation in this beaker can be regarded as finished. The residue from II. is united with that from I., and filtered, dried, and weighed. The resulting weight gives the quantity of the impurities present in the original sample.

The glass beakers III. and IV. contain the pure colour, held in suspension in the water, that in No. IV. being in a finer condition than the other. In this way the product can be classified into grades of different degrees of fineness during the process of levigation, the number of grades varying directly with the number of beakers used. Of course, the larger the number of vessels the longer the time consumed, and therefore the greater the expense. For this reason it is seldom that more than four vessels are used for the levigation of natural mineral colours.

When the colour in the beakers III. and IV. has settled down sufficiently the clear water is poured off, the residues are collected on separate filters, and the resulting pasty masses are dried in the drying-room. According-ing to their specific properties, the various grades of dried colour form dense, compact lumps or loose masses easily crushed by the finger; and these, after being weighed, are ground in a mortar, and finally sifted through a fine sieve. The quantity of the powder obtained is also ascertained by weighing; and by this time all the data necessary for an exact calculation will have been obtained, namely:

(*a*) The moisture content of the raw product.

(*b*) The useless impurities, such as earthy particles, sand, small stones, humus, &c.

(*c*) The weight of the colour after levigation and drying; and

(*d*) The weight after crushing and sifting.

From (*c*) and (*d*) can be calculated the approximate loss of colour sustained by grinding and sifting.

If the raw material as it comes from the mine is so pure or of such a hard and stony nature that the tedious process of levigation can be dispensed with, or is impracticable, the material is crushed in the dry state, the residues left after sifting being recrushed in the mortar and sifted anew as often as is found necessary. The finally uncrushable residue is weighed, and the calculation is based on the weight obtained.

In the examination of many coloured earths, and especially the crystalline stony kinds, it is highly important to note what changes they undergo in colour and structure when calcined. Most yellow and brown earths or minerals alter in tone at high temperatures, turning reddish or pure red, whilst the natural reds become much brighter when heated, others, again, changing from grey to deep black. At the same time heat effects a conspicuous change in the structure of the crystalline or stony minerals, inasmuch as on cooling they crumble to a moderately fine powder, either spontaneously or under the application of comparatively slight pressure. This change of structure is in most cases accompanied by an increased covering power, especially when the red-hot lumps are suddenly thrown into cold water. This very sudden cooling-off—known in practice as "quenching"—causes even the hardest crystalline minerals to crack, and for this reason the treatment is sometimes applied for pulverising hard kinds of rock, such as quartz, barytes, &c.

Generally the heating of the earthy raw materials is performed on the small scale either in clay crucibles or on a thick sheet of iron. The change of colour is noted, and when this ceases the materials are taken from the fire and the mass is thrown into cold water, or is left to cool down gradually in the air. The usual plan is to try both methods side by side, and compare the results in respect of the colours and covering power of the products.

In building works for the preparation of natural mineral colours the question of situation is of the greatest importance. On the one hand, a considerable saving in freight—a very important item in view of the low price of the manufactured goods—can be effected by erecting the works in the immediate vicinity of the place where the raw materials are found. On the other hand, the works should not be far away from the main lines of communication (as railways, shipping, &c.), in order to secure favourable rates for the conveyance of the finished colours. The circumstance that the expense of steam power can be dispensed with in manufacturing natural mineral colours makes the presence of a sufficiently large supply of running water desirable, large quantities being required not only for driving the numerous machines, some of which are heavy, but also for the levigation process. As regards locality, three main points come under consideration, but these can seldom be harmonised, and consequently most works for the treatment of natural mineral colours now deal only with certain special brands, or (more frequently) are run in connection with the production of artificial mineral colours. The most influential factors are proximity to the place where the raw products are found and the presence of sufficient water power. The latter, in consequence of its cheapness, is most important in determining the cost of production. These conditions can generally be fulfilled, especially in mountain districts, where, moreover, the raw materials are chiefly to be found.

As to the erection of the factory, the experimental trials described above indicate the necessity for grinding and sifting plant, which can be mounted in one room; and, in the second place, the provision of a separate room for levigation. At least one calcining furnace will be required, together with drying-rooms, heated artificially or otherwise. The stipulations already laid down as to the arrangements for the manufacture of artificial mineral colours (pp. 11–13) are also applicable to the various departments in natural mineral colour works, so that we have now only to consider a few points referring specially to the class of work under consideration.

The *grinding room*, containing the edge-runners, ball mills, and the heavy balance mills, should be as large as possible, and well ventilated. The production of dust, though less injurious to health than with artificial mineral colours, may at times prove very troublesome in practical working, and therefore dust-removing appliances are highly desirable. For the same reason the grinding room should be as light as possible, and should be fitted with top lights as well as windows. A separation of the various groups of colours is advisable, it being essential that the white natural mineral colours should be ground apart from the rest, even when the latter are very light in colour. The *packing-room* must be in immediate proximity to the grinding-room, to avoid unnecessary loss of time in the transport of the ground product. In many works the finished colours are packed in the grinding-room itself—another reason for making this room as large as possible.

If, as is generally the case, the *levigation* of the natural mineral colours is performed in closed rooms, these should be of ample size, and above all be extremely well lighted, a top light being best. The levigating-room must have a sufficient supply of water, and a very well laid floor, so that any overflowing water can be properly drained off through one or more gutters. The other details of this room will be described in the following chapter, which deals more directly with the levigation process itself.

The *calcining furnaces* must be put up in special departments—separated from each other—on account of their method of working, and also, as a rule, because of their very large dimensions, so that they can be accessible from all sides. This circumstance alone necessitates plenty of space, and this condition is accentuated by the considerable quantities of material that have to be treated in the works. In order to save fuel by recharging the calcining ovens as quickly as possible, a large supply of the raw materials must be stored in readiness near the ovens; and also a large space must be available, preferably in the calcining house itself, for cooling down and quenching the roasted charges. The construction of the furnaces and the other arrangements of the calcining room will be more minutely discussed in dealing with the calcination process.

A drying-plant is only required for products that have either passed through the levigation process or can be ground in the crude state. The circumstance that the natural mineral colours can stand a tolerably high temperature without undergoing any change appears to admit of the application of drying arrangements such as are described in connection with the artificial mineral colours; but, on the other hand, the larger quantities to be treated, and their low trade value, indicate the advisability of simple arrangements and a greater command of space. The drying of the natural mineral colours and their crude products is therefore preferably effected in the open air, in which case it is only necessary to afford sufficient protection against atmospheric moisture, rain, &c. Hence the site for a natural mineral colour works should be one that is exposed to the sun as many hours as possible per day. In larger works, however, the great extra space entailed, where open-air drying is the sole means employed, is inconvenient, and for this reason artificially heated drying-rooms are also provided. These appliances, which are described more fully in the chapter on drying natural mineral colours, must be situated in close proximity to the grinding-room, and if this is not feasible should be connected with the same by rail tracks, the dried materials being loaded into trucks for conveyance. Similar arrangements are advisable for the transport of the raw and levigated products dried in the open air.

II.—THE CHIEF PROCESSES IN THE TREATMENT OF NATURAL MINERAL COLOURS

a. Levigation Process and Apparatus

The levigation process, the principle and object of which have been already explained (p. 348) in the description of the preliminary experiment, generally requires mechanical power for its successful application; and the rapidity and economy of the process are increased with the number of apparatus and appliances used, and the more suitably they are arranged and utilised.

In place of the glass beakers used in the preliminary experiment, levigation on the large scale is performed in wooden vats or iron tanks of suitable size. The preliminary working or softening of the raw materials is effected (according to their nature) either in large wet mills, as illustrated in Fig. 9, or in vessels fitted with vertical or horizontal stirrers running at a high speed. These last-named machines are situated opposite to the vats or iron tanks, but on a higher level, the levigating vessels being generally mounted in terraced rows, so that the contents flow through an opening made in the upper rim of one vessel into the vessel next below.

The work begins by running a certain quantity of water into the wet mill or stirring machine, the runner being set in motion and a weighed quantity of the raw material for levigation gradually admitted, after which the mill is run until the raw materials have been thoroughly separated and softened. A continuous thin jet of water is next allowed to run in, without stopping the mill, thus quickly filling the vessel so that the contents overflow through a short gutter into the adjoining lower vessel, I., at the same rate as the incoming jet of water.

In this proceeding the baffle, *D* (see Fig. 9), plays an essential part, inasmuch as it not only prevents the finer detached parts of the material from settling, but also forces them by a continuous jerking motion through the gutter into the vat I., whilst the coarser, incompletely detached ingredients —viz., the impurities, sand, small stones, &c.--fall through the broad part of the baffle by their own weight down between the stones, and are thus crushed again. The quadrangular gutter, open at the top, is fixed into an opening of equal size in the mill-casing, *C*, in such a manner that the upper rim of its sides is on a level with the upper rim of the mill-casing at the other end, sloping down to the rim of the vat I., and projecting about four inches into the interior. The other vats, usually three to four, are connected together in the same manner. Before the levigated material reaches vat I. it passes through a fine sieve in order to keep back any small fragments of wood and straw (always present in earthy raw materials) floating on the surface of the water. This small sieve is hung directly under the outlet of the gutter leading from the mill to vat I., and can be kept in continual motion by a jigging device In order to prevent the flow being obstructed by the accumulated small particles of earth, the sieve must be cleaned out from time to time. The described arrangement of the connecting gutters indicates what difference of level must be arranged between vat I. and the wet mill and between vat II. and vat I. in order to enable an equal flow to be maintained from one vessel to the other. In no case need this difference exceed twice the depth of the gutter, so that it is evident an efficient levigating plant can be put up without requiring excessively lofty rooms.

When it is noticed that the water flowing through the gutter to vat I. is clear or nearly so, the water-supply is stopped, and the plug on the other side of the mill-casing is opened, whereupon the impurities in the mill are ejected by the movements of the runner. When the liquid in the mill has fallen to the original level the plug is driven in again and the mill is recharged, the cycle of operations being repeated until all the vats are filled.

The contents of the vats being in a state of almost perfect rest, the coarser particles of material will settle at the bottom when vat I. is full, whilst on the flow being resumed another part runs over into vat II., so that the contents of vat II. represent more finely divided particles of colour than those in vat I. A similar but less marked difference in fineness exists between the contents of the remaining vats, so that the end one of the series contains the most finely levigated colour. Apart from the quantity of material and number of vats, the duration of the process depends also on the character of the raw material, some influence being also exerted at times by the form of the vessels. With earthy raw materials of low specific gravity the process is greatly retarded unless a large number of vessels are used. This delay is particularly noticeable in the levigation of many ochres, and certain brands of umber which are of a clayey nature as well as of low specific gravity. Conversely, with specifically heavy raw earths the process goes on too quickly, owing to the rapid deposition of the particles, so that the contents of vat I. have frequently to be milled over again.

In the levigation of specifically heavy materials, such as the iron red from roasted pyrites (see "Sulphuric Acid"), the stirring device mentioned at the beginning of this chapter is sometimes used. In this case, however, the materials are not ground in wet mills, but the finer particles present are merely separated from the coarser ones. Since these latter always settle to the bottom quickly, the operation proceeds with great rapidity, and considerable quantities can be treated in this manner in a comparatively short time. The apparatus suitable for this purpose consists of a box made ot thick boards, 40 ins. in length, 20 ins. in breadth, and 20 ins. in height, in which a horizontal iron or wooden shaft rotates at high speed. On both of the narrow sides of the apparatus is a round opening, through the smaller of which, at a somewhat higher level, the levigated particles escape, whilst the lower one, about twice the size, drains away the residue. The materials for levigating are shovelled into the box, into which flows at the same time a continuous and fairly large jet of water. The mass is acted upon by the vanes mounted on the shaft, and after the finer particles have been carried off by the outflowing water the sediment falls to the bottom of the apparatus at once. The accumulated residue is ejected in the form of a thickish pulp out of the lower side opening by the action of the vanes, and falls into a receptacle underneath. The finely levigated material is led into shallow, square iron tanks arranged in terraces in adjoining rows, and connected with each other by gutters, the particles settling more or less quickly to the bottom. The apparatus is not so good for specifically light raw earths, since it works too rapidly, but has the advantage of being easily set up by reason of its simple construction—for instance, at the pits, where it renders excellent service in the rapid levigation of certain ferruginous (red) gravels. For this purpose the dimensions must be somewhat greater, especially the height, so as to provide greater space for the deposition of the residue, which is then removed from time to time through a side opening fitted with a plug.

In order to save room, both in width and depth, in the levigation of very light raw earths with an increased number of vats, it is more practical to retain the four-vat system, always using two, however, and, if necessary, three, rows of vats, connected with the wet mill, whereby twelve vats can be worked at the same time. Owing to this simple distribution of work, very considerable quantities of raw materials can be treated in a comparatively short time. To maintain a uniform output a somewhat large number of wet mills, each with a system of vats, must be put up in the levigating room, by constructing along one side of the room a platform of strutted beams, measuring about 8 to 10 ft. in height and the same in breadth, upon which platform the wet mills are set up at certain distances apart in a row. The intermediate spaces are boarded over with thick planks. Steps are provided between the mills, and between these steps the vats are mounted in terraces on correspondingly high and firm timber supports. The height of the tanks must correspond to that of the platform, and this, again, to the height of the space at disposal.

When all the vats are filled with the levigated colour they are left alone until the solid matter has settled down sufficiently, whereupon the clear supernatant water is drawn off from each vat, and the solid deposit is removed. The manner in which this work is performed again depends on the nature and peculiarities of the colour itself. Whilst specifically heavy natural mineral colours generally form a fairly stiff paste which can be at once spread out to dry, the lighter colours, and especially the clayey ones, must first be filtered and pressed. Since this operation, as in the case of the artificial mineral colours, is attended with great difficulties and loss of time, and, indeed, in the case of certain natural mineral colours cannot at times be performed at all with the ordinary appliances, large chamber filter-presses (without flushing device) have recently come into use for filtering and pressing natural mineral colours, with the greatest success. Two or three of these filter-presses are arranged in the levigating-room in such a manner that each one can be filled from three to four sets of vats.

Some materials which, though not used as colours, are usually prepared in colour-levigating works on account of the difficulty experienced in grinding them in dry mills, are treated in very large wet mills, the stones of which have a diameter up to 10 ft. and are built up of separate pieces (by means of iron clamps and molten lead). In other respects the construction is just the same as the wet mills shown in Fig. 9, and their action is usually the same.

The materials in question (talc, china clay, &c.), are wet ground in these mills to an impalpable powder, which is then treated in the same way as natural mineral colours, excepting, of course, as regards the dry grinding.

b. Drying Natural Mineral Colours, and Drying-Plants

Drying-plants may be divided into two classes, one serving for drying the raw materials and the other for drying the levigated colours. Whereas for the former purpose very simple arrangements generally suffice, by reason of the low content of moisture in the raw materials, the levigated colours require special drying appliances, on account of their more or less pulpy nature, which in many points are similar to those used in the manufacture of certain artificial mineral colours.

As to the *drying of the raw materials* which are suitable for direct grinding, the natural warmth of the sun would generally suffice (if the situation of the factory permitted) to dry the materials far enough to facilitate grinding, were it not that drying in the open air depends too much on the time of year and changes of weather—a circumstance which may cause very considerable trouble, especially in large works. Hence the construction of artificially heated drying-plant, which must not only be equipped with convenient means for charging and emptying, but also be sufficiently roomy.

The best type of drying-room is a large, but not too high, fireproof room, the flooring of which is provided with a system of flues, about 8 to 12 ins. wide and deep, entirely covered with cast-iron plates or firebrick tiles. The flues are connected with a fireplace, which is mostly placed in the cellar, and are so arranged that the draught flows into a main flue and thence into the chimney. The arrangement is thus similar to that already described for ultramarine blue, and illustrated in Figs. 60 and 61. The raw materials to be dried are spread out with a hoe or shovel as evenly as possible on the hot floor. By frequently turning the mass (it being advisable in the case of soft, earthy masses to break down the large lumps roughly) drying proceeds quickly, and even in the case of very damp materials and the most unfavourable circumstances is complete in less than twenty-four hours. A similar room can, of course, be used also for drying the lumpy levigated products from the filter press.

For drying the more pulpy or very fluid levigated natural mineral colours this arrangement is, however, less suitable, and many works use special drying-hearths, about 40 to 60 ins. wide, arranged along at least three sides of a closed room. These hearths form the top of a flue about 40 ins. wide and high, extending from the fireplace to the entrance of the actual chimney. The flue cover, which forms the hearth, is constructed of thick fireclay plates, and provided with a border about two bricks high, so as to prevent the pulpy materials running over the edge and to allow of their being turned over and over. When they have been dried to the condition of more or less moist lumps they can be finished on the usual drying-floor, and the hearth recharged with wet material. The plant is of high capacity, and consumes only a comparatively small quantity of fuel, coal being used in preference to coke.

In many works the waste gases of the calcining furnace are utilised for drying both the raw materials and the levigated product in the same manner as explained for ultramarine (see Figs. 60 and 61); but this pays only when the calcining furnace can be kept at work continuously, or nearly so. The heating value of the waste gases from the calcining furnaces can be more effectually utilised by leading them over the raw materials spread out in special vaulted rooms, provided with openings for charging and emptying, and floored with brick or fireclay tiles. The drying-chambers are built close to the calcining furnaces, and are separated from the hearth merely by a partition with a sufficiently large opening for the hot gases. The opening is fitted with a damper, which is only withdrawn when it is certain that the hot gases are free from smoke and ash.

When the extent of the works admits of it the drying-flues, described on p. 50, can be successfully used for drying the crude as well as the levigated products. Also, in factories where steam power is available use can be made not only of the steam drying-plant, but also of such as can utilise the hot gases from the boilers. The necessary conditions are ease of access and a large surface, so as to obtain a maximum efficiency, because the low price of the natural mineral colours does not easily admit of the use of complicated arrangements unless these can be also utilised for subsidiary by-products.

As regards open-air drying-plant, the wooden racks illustrated in Fig. 32 are found to be the best for drying natural mineral colours and their raw materials, since they can be easily roofed over as a protection against the rain. In place of the lath fittings, shallow box-like trays are used for the pasty or still more liquid levigation products. These trays slope gently from the middle outwards to the two long sides, so as to drain off the water more quickly and to facilitate emptying the racks. The wider the latter are made the greater is the distance between the trays carrying the damp materials, and the easier the filling and emptying of the racks. The increased distance ensures a more effectual circulation of air, and this materially assists the drying process. Of course, the wider the racks the stronger must th be made.

The factory lofts may be fitted up for use as drying-rooms for the l damp raw materials, the latter being spread out on the floor, and mea taken to ensure effectual ventilation of the room.

c. Methods and Appliances for Pulverising, Grinding, and Siftir Natural Mineral Colours

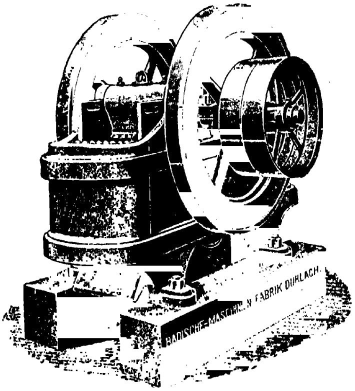
The important operation of pulverising is, in the main, the same for a natural mineral colours, whether these be the dried raw materials or tl levigated or calcined products. Generally the sole difference consists in tl use of differently constructed machines, which must be adapted to th physical peculiarities of the substance to be treated—*i.e.*, their relativ hardness or clayey nature, the latter greatly increasing the difficulty (grinding and sifting.

In any case, in consequence of the low commercial value of the natur mineral colours attention must be chiefly directed to securing the highes possible output per diem, so as to avoid overloading the cost of productio by superfluous charges for wages; and this object can only be accomplishe by using machines of the highest possible productive power. Whilst a fe years ago it was thought feasible to work with very primitive pulverisin machinery, well-equipped factories are now provided with such extensiv mechanical appliances that at first sight their prime cost seems to be out o all proportion to the commercial value and profitableness of the products This is, however, not so, for the conviction is gaining ground that the mos perfect appliances for pulverising, and the adoption of systematic workin throughout, can, in spite of the high prime cost, successfully compete wit the more primitive appliances, owing to the higher proportional outlay o labour entailed by the latter. Such high-class plant, moreover, has become a necessity, owing to the more exacting requirements of consumers in respec of the fineness of the colours, so that both increased output and greate fineness have to be considered.

As with the artificial mineral colours, the pulverising of natural minera colours is divided into three stages, namely, *rough grinding*, *fine grinding* and *sifting*. These operations can be accomplished either separately, o all three can be combined by the aid of the aforesaid extensive machinery worked systematically. For reasons already given, the latter plan is the one now generally adopted, and it is therefore preferable to omit discussion of the obsolete and primitive methods and arrangements, and to describe the more complete process in accordance with the new method, the more so because any one desiring simpler forms can devise them for himself from the particulars given to suit his own taste or the size of his works.

The method of pulverising and the selection of the requisite machines chiefly depend on the relative hardness of the material. For such raw materials as are pure and soft enough to be ground direct, large milling tones or ball mills may be used, like those illustrated in Figs. 44 and 52–55. Harder raw materials have first to be rough-ground with large and heavy edge-unner mills, the runners of which are generally of iron. Very hard crystalline minerals, such as barytes, iron-stone, slate, &c., must first be treated in crushing machines or stamping mills, so as to reach the edge-runners in the form of small bits, and pass thence to the mills. The ground material rarely needs sifting, since generally even the hardest minerals can be reduced by one or more millings to a powder fine enough to satisfy all requirements of consumers. The grinding of the natural mineral colours to the highest degree of fineness is the more feasible since they do not suffer any change through the heat generated by friction in the mill. This method is also more profitable from a pecuniary point of view, since with most natural mineral colours the cost of production would be much higher if sifted, owing to the considerable difficulties experienced in passing them through fine silk or wire gauze, and the consequent diminution of the output. For many purposes, however, sifting is unavoidable, and this operation, which differs in no way from that described for the artificial mineral colours, will therefore be dealt with in each case where it has to be employed.

FIG. 79.



The mills and ball mills having been already fully described on pp. 56-60 and 64-67, we need only deal now with the crushing machines and stamping mills, with which the preliminary crushing of the hardest minerals is effected.

FIG. 80.

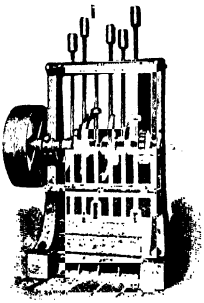
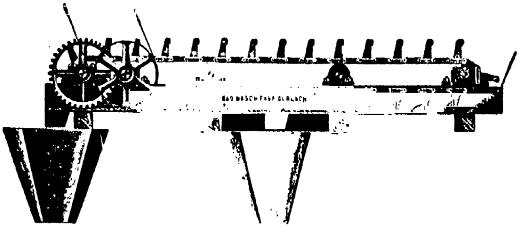


Fig. 79 shows a Black's stone-breaker, or "jaw" crusher, a very heavy machine, which must be mounted on a special foundation on account of its considerable weight. The mineral, in lumps the size of the fist, on being thrown into the mouth of the crusher are caught between two coarsely grooved, heavy steel plates, and are smashed to pieces by the pressure. Since one or both of these plates are set in such a position that the mouth of the crusher tapers conically downwards, the materials already broken are pulverised still more as they fall down lower, and finally escape at the foot of the machine as a coarse-grained powder. The size of the pieces that can be treated in these crushers is limited only by the width of the crusher's mouth. On the other hand, the fineness of the broken materials can be regulated between the limits of 2¼ and ⅘ in. With the increasing fineness of the broken material the production of fine meal increases, and the output is lessened, on which account the crusher is generally set to yield fragments not less than 1 in. in diameter.

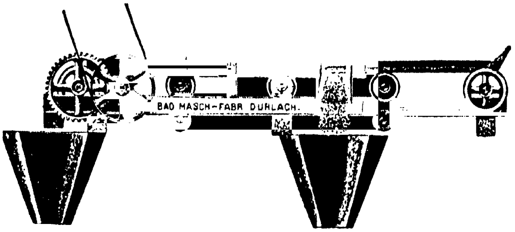
Besides stone-breakers, many works employ *granulators*, which closely resemble the crushers, differing, however, in being able to deal with the coarser grains, such as are furnished by the stone-breakers, and reduce these to a fine sand without any loss of productive capacity, the action being a combination of crushing and tearing, and the crushed material being ejected at once, without any troublesome reduction to meal or excessive formation of dust.

FIG. 81.



The *stamping mill* illustrated in Fig. 80 consists of an iron frame with trough and shaft, and a number of stamp heads, which are alternately raised by the cams on the shaft and allowed to fall down freely. The stamp-heads and troughs are of hard or chilled steel. The stamps rotate freely during the up-stroke, so that the wear and tear is equalised. The materials to be pulverised are fed into the trough, and are quickly pounded to the requisite fineness.

FIG. 82.



According to requirements, the troughs may be closed, fitted with a sifter, or arranged for levigation.

By the rough crushing of less hard, though not sticky or clayey masses, the machines illustrated in Figs. 39, 40 and 42 do very good work, and are therefore very frequently met with in the manufacture of natural mineral colours. To maintain a regular and economical system of grinding, the chief point with most of the natural mineral colours is to correlate the rough crushing with the subsequent fine milling (which, as already observed, must be repeated three to four times) in such a manner that the conveyance of the mass from one machine to another is effected by mechanical means in certain regular progression.

The various pulverising machines, stone-breakers, edge-runners, an mills, should therefore be set up in the manufacturing room in such a manne that they can be combined whe necessary without difficulty or circuitous means. Communicatio between the several pulverisin machines is effected by means o conveyors, which carry the pulverised materials in a horizontal o ascending direction, according to the relative position of the machines. Th conveyance of the mass in a horizontal direction when long distances ar involved takes place by means of endless belts with or without small scoop (see Figs. 81 and 82), or for shorter distances by means of endless screw (Fig. 83), the arrangement and method of working which is easily discernible from that figure. For transport in an oblique or vertical direction the chain and belt elevators illustrated in Fig. 84 are used exclusively.

FIG. 83.

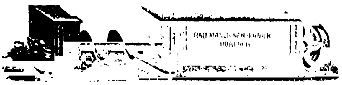
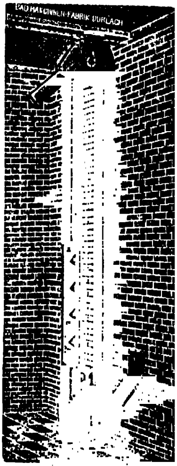


FIG. 84.



With all these apparatus it is essential that the moving parts should be placed in wooden or tin box-shaped casings or covers, closed at the top, and that the materials to be conveyed are not of a very sticky nature, otherwise troublesome obstructions will be produced, sometimes stopping the machine completely. The conveyors between the various pulverising machines are so disposed that they can be easily and conveniently driven by pulleys and driving-belts from the main shafting, and, if necessary, can be thrown out of action at once. In this manner a certain special set of apparatus can be arranged for each colour, according to its relative hardness, so that the material need only be fed to the rough crusher, and, after passing all the other intermediate machines which continue the reduction, finally leaves the mill in the form of a sufficiently fine powder ready for sale. With materials needing repeated grinding, such as barytes, the machines are so arranged that after the mass has passed the edge-runners and the adjacent mill it can be conveyed to a second, third, and, if necessary, a fourth mill without difficulty. For this purpose all the mills in each room are mounted on the same level. They may either be placed in rows along the wall, in which case the crushing machines and edge-runners stand side by side at the ends of the row, or two or three mills, or more (according to the size of the works), can be set up at opposite ends of the room, sufficient space being left between the rows for other work. The crushing machines and edge-runners are then preferably set up at the end of this space, next to the entrance of the drying or store room, in such a way that they can be conveniently fed without obstructing the conveyance of the material to the mills (if possible on both sides at once). All these machines, except the crushing machine, are preferably driven from below, and by means of a central overhead shafting parallel to the two rows of mills, and transmitting power through driving-belts at the dead end of the room to the two lower driving-shafts.

By this arrangement the narrow driving-belts for the various conveyors can be mounted on the main shafting without risk to the workmen.

Materials (*e.g.*, most of the levigation products) which need only a single grinding and cannot be pulverised finely enough for trade purposes in ball mills, a preliminary squeezing of the soft lumps with edge-runners and feeding the resulting medium powder to the adjacent mill is generally sufficient, and therefore the conveyor between the breaker and the edge-runner can be thrown out of action if its construction permits, and the breaker meanwhile be used for other purposes.

In discussing the levigation process it was mentioned that the general levigation tanks contain products of different fineness, and the pulverising, of the dried grades will differ accordingly as the contents of all the tanks are treated in combination or separately. In the former case most natural mineral colours generally require a thorough dry grinding in the stone mill, and only in the rarest cases will grinding in the ball mill alone be sufficient and suitable. If the contents of each single vat are dried separately the invariable plan is to grind the products coming out of the two vats I. and II. (those next to the wet mill) in a stone mill, whilst the finer products coming from the vats III. and IV. can be mostly reduced to a sufficiently fine powder in a ball mill. In other respects no comprehensive rules can be laid down in this place, generalities alone being discussed, and the matter must therefore be relegated to the chapter dealing with the single earth colours.

d. The Chemical Treatment of Natural Mineral Colours – Calcination, and the Resulting Physical and Chemical Changes – Calcining Furnaces

Calcination is the treatment of chemical compounds at high temperatures, either by themselves or in admixture with other bodies capable of producing an oxidising or reducing effect. In calcination the substance undergoes a change which may be both chemical and physical. Thus the immediate consequence of the calcination of most crystalline salts is the loss of water of crystallisation, the salt only changing its exterior form, without undergoing a chemical decomposition. At high temperatures many metallic hydroxides lose their chemically combined water (water of hydration), and pass over for the most part into the corresponding oxides, which latter, if in a high stage of oxidation, sometimes give off a part of their oxygen when the temperature is raised still higher. A large number of salts which have already lost their water of crystallisation by calcination lose with continuous heating their acids as well, the latter being mostly degraded to lower stages of oxidation, with liberation of oxygen, whilst the metallic oxides are left behind as calcination products.

Furthermore, certain minerals or earths serving as natural mineral colours undergo an essential change on calcination, which change may relate to their appearance or molecular form, or to both at the same time. The change in molecular form is generally, but not always, accompanied by a change of tone; its direct consequence is a more or less noticeable condensation of the material, the result of which is manifested by the increased covering power of the calcined product. This remarkable phenomenon is attributable to the circumstance that the expulsion of the water of hydration causes the molecules in the compound (generally a metallic oxide) to occupy less space, so that they draw closer together, and the phenomenon of "contraction" occurs. The usual, but seldom very considerable, change of tone produced by calcination appears to have some relation with the change of molecular form, although many instances are known which directly contradict this view. Apart from the white mineral colours, such as artificial barytes, the covering power of which is greatly increased by calcination, certain iron oxides—for example, the decomposed spent pyrites from sulphuric acid manufacture—do not change colour in the slightest after the most violent heating, though their covering power is improved. The brighter tint sometimes noticed in the calcination products is due, not to any change in molecular form, but to the decomposition of green copperas (ferrous sulphate) formed by the decomposition of the spent pyrites. If the latter is refined by leaching out the sulphate with water it undergoes no further change of any kind apart from the aforesaid increase in covering power.

Conversely, the changed tone of calcined natural mineral colours is not always necessarily connected with an increase or decrease of the covering power—*i.e.*, according to the theory now under consideration, with a change of molecular form—other cases being known wherein an increase of covering power and other associated physical changes (such as increased specific gravity) are no longer observed, although an essential change of tone occurs. An example of this is afforded by the "caput mortuum" (colcothar) formed as a secondary product in the manufacture of fuming sulphuric acid, this product, under certain conditions, showing no increase in covering power, although it undergoes essential changes of tone on calcination.

If we pass in review, after these brief introductory remarks, the series of those natural mineral colours which can be improved in manufacturing and commercial value by a suitable calcination, we find that above all others the numerous *ferric hydroxides* and basic ferric sulphates seem to render profitable the cost of calcination and of the extensive plant needed for that process. This applies more particularly to the various ferric hydroxides, chief among them being the brown hæmatites, $H_2O.Fe_2O_3$ to $3H_2O.Fe_2O_3$, and bog iron ore. These, whilst naturally perfectly insignificant in colour, are changed under certain circumstances by calcination into a very fiery red, the covering power of the products being considerably increased. This change is based on the loss of water of hydration at higher temperature, and the formation of an almost pure ferric oxide, with all its favourable pigmentary properties. The various native *ochres* also consist essentially of ferric hydroxide (more rarely basic ferric sulphate), associated with larger or smaller quantities of aluminium silicates as impurities. The presence of these latter influences the shade of the more or less reddish-coloured products obtained on calcination. Hence these mineral colours are not changed in tone and covering power by calcination so much as the above-named pure ferric hydroxides, since the alumina and lime and manganese compounds accompanying the latter are also modified by calcination, and these alterations are communicated to the resulting ferric oxide. Whereas the alumina and lime compounds, according to their quantity, chiefly lower the covering power of the calcined or "burnt" ochres, the naturally brown manganese compounds change the tone of the calcination products to a more or less brownish hue, the colour of the manganese compounds being rendered considerably brighter by calcination. The natural mineral colours that are stained yellow by ferric hydroxide (which, together with manganese hydroxide, forms their chief ingredient) become almost pure red to red-brown after calcination. In proportion, however, as manganese hydroxide preponderated in the natural composition of the compound, so does the tone of the calcination product change more and more from red-brown into brownish red, and finally into pure brown. To this latter class of natural mineral colours belong the numerous and widely distributed varieties of natural *umber*, the brown shade of which on calcination is purer the less ferric hydroxide and other pigmentary impurities they contain. Such earth colours are put on the market as *burnt umber, manganese brown, velvet brown, chestnut brown*, &c. . . .

Furthermore, many *clays*, among these the *slate-clays*, or shales, turn grey on calcination in consequence of the loss of mechanically admixed or chemically combined water; and, as is mostly the case, if they also contain ferric hydroxide a reddish grey tint is produced, the structure being also so essentially modified that they sometimes furnish colours with fairly good covering power suitable for grounding purposes. Natural mineral colours of this class possess in a high degree the property of forming with linseed oil varnish very hard-drying, and therefore extremely durable, coats of paint. They are therefore used preferably as grounding colours for other coloured paints or for filling up inequalities in the surfaces to be painted. The product known in the trade as *filling-up* belongs to this class.

As regards the furnaces used for calcining natural mineral colours, *reverberatory furnaces* of the simplest construction are evidently most suitable for this purpose, since they are used almost exclusively in natural mineral colour works at the present time. The arrangement of a reverberatory furnace is in the main as shown in Figs. 73 and 74, only that in the present case the hearth of the furnace, instead of being depressed as shown in the figures, must be perfectly level. The fireplaces may be at the sides or in front, and below the level of the hearth, a low stone-work bridge, over which the flame passes, separating the hearth from the fireplace in either case. More frequently, however, the fire is placed at the side, though there is no special reason for this arrangement, except, perhaps, that it facilitates charging. As a rule, the calcining furnaces for natural mineral colours need not be of such a large size as the lead oxide furnaces illustrated in Fig. 73 and 74, or of such massive construction as is there necessary, the calcining process being a less protracted operation in the present case, so that the furnace can be charged more frequently. It is necessary, however, that the flattened vault in the thicker side walls of the furnace (which, when necessary, are held together by a strong iron framework) should have a sufficiently firm and safe support. The charging and emptying apertures are arranged at the sides when the furnace is fired from the end, and *vice versâ*. In order to enable the calcination products to be thoroughly raked over (which is always necessary) in furnaces of larger size, special openings are still frequently provided in the back wall of the furnaces for the insertion of the rakes. In this manner the colour in the furnace can be sufficiently raked over from the side—*i.e.*, from the front as well as from the back, and especially long, heavy iron rakes are, in this case, not necessary.

The charge corresponds to the dimensions of the furnace as well as to the peculiarity of the minerals in question, on which also depends the duration of the calcining process. The form of the material is the chief factor—whether it is in coarse pieces, in grains the size of a nut or smaller, or in the state of powder. The latter form is generally the most suitable, since it ensures earlier completion of the process, and thus effects a considerable saving of time and fuel. Whenever the hardness of the minerals admits, the materials should always be pulverised sufficiently in a breaker or stamp mill, or by edge-runners. In whatever form the material to be calcined may be, it must not be spread too thickly on the furnace hearth, since that not only retards calcination, but also makes the raking of the mass unnecessarily difficult. When the minerals are in fine powder care must be taken to prevent any strong draught in the furnace, or a considerable part of the material may be carried away into the flue, and cause trouble in working, apart from the direct loss sustained thereby.

The time required for the calcination of one and the same material when the furnace is heated continuously often varies only within narrow limits. Much, however, depends on the construction of the furnace itself, and on the use of uniform quality of fuel. No definite guidance can be given in this respect. When the object of the calcination process is accomplished, which can be ascertained by taking samples from time to time, the hot, sometimes glowing, mass is raked out of the furnace through the discharge openings and left to cool in large iron chests or in special fireproof places. Should it be necessary to cool the red-hot product suddenly by means of cold water, this can best be done by raking out the mass direct into suitable iron tanks filled with water. The hot or still glowing heap must on no account be sprayed with water, owing to the great risk of accident thereby entailed; and for the same reason the throwing of the mass into water must be performed with the greatest care.

e. Mixing the Natural Mineral Colours

As with artificial mineral colours, the attainment of a certain shade often entails the mixing of two or more colours; in fact, it may be said that this operation is more important in the case of the natural mineral colours than with the chemical colours, for whilst in the latter case there are always ways and means at hand for facilitating the attainment of the end in view, a limitation is set in the case of the natural mineral colours by the available material, which varies according to circumstances. Other circumstances also combine to add importance to the mixing of natural mineral colours. Owing to the considerable increase in the number of shades of these colours on the market, each maker must, if he wishes to compete, produce the whole series, in uniformly good quality and appearance; and as all makers cannot draw on the same sources of raw material, it becomes necessary to resort to mixtures of the raw materials or finished products they have at disposal.

Generally speaking, the price is the determining factor. On the other hand, many factories, in the course of time, owing to the ever-increasing competition, have undertaken to supply mixtures which formerly were prepared by the consumers themselves, such as colours for wall-papers, floors, façades, &c.; and this, of course, increases the number of grades turned out by each individual maker. This led to the necessity of extending the plant and putting down more efficient machinery, in order to cope with the increased demand, which circumstances again led to the opening up of new sources of supply and the discovery of new raw materials and methods of preparation. Chief among the latter must be classed the manufacture of the red ferric oxide colours, which for a long time were mainly obtained from England, but are now very largely produced in Germany, of considerably better quality and brighter shades, from bog iron ore and brown hæmatite. These new colours and their much cheaper price enabled a large number of new mixed colours to be produced for a large variety of technical purposes—among others, floor-stains, façade and weather-proof paints, &c. With these also became associated a great number of mixtures with the artificial mineral colours, such as chrome ochre, bronze brown, olive green, &c., or with certain lakes from vegetable colours, *e.g.*, quercitron yellow, palm yellow, leather yellow, &c.

All these mixed colours are prepared by mixing the components in a dry state, but seldom from the raw materials direct, the ready-made colours, ground at least once, being preferred as more reliable. The mixing is effected either with edge-runners or in shallow iron pans or large wooden boxes with shovels, the materials being turned over and over until they form a uniformly coloured mass, which is then worked in a large ball mill for more thorough mixing, or is run through a millstone several times if necessary. The mixture can be regarded as complete when a sample of the product smoothed out with a horn or steel palette knife forms a uniformly coloured mass—*i.e.*, none of its ingredients can be detected in the mixture.

The mixing of the single natural mineral colours, either together or with chemical colours, requires a thorough knowledge of their physical and chemical properties, and more particularly of their colouring action, and can therefore only be performed by experienced colourmen. It being difficult to determine the individual ingredients of such mixtures by qualitative analysis, in the absence of artificial mineral colours, it is impossible to analyse them quantitatively. Hence the colourman has in most cases only his experience and his practised eye to depend upon when confronted with the task of imitating a given mixture in quality, tint, and price. In consequence of the great multiplicity of mixtures from earth colours known in the trade, no general rules can be given here, and it therefore seems more expedient to defer the treatment of the points in this connection to the description of the individual groups of colours given later on.

PART II

I.—WHITE EARTH COLOURS

a. THE NATIVE BARIUM COMPOUNDS

Barytes (*Barium Sulphate, Schwerspath, Sulphate de Baryte;* $BaSO_4$)

BARYTES occurs generally as more or less large masses only in the primitive rocks or in those of volcanic origins. In Germany especially it is found in fairly considerable quantities and mined in several places. It is chiefly found in the Oden forest (Hesse), near Neustadt, in the Spessart, near Lohr-on-Main, Waldshut (Baden), in Thuringia, near Koenigsee, &c., sometimes in great abundance. It occurs in various forms and degrees of purity, ranging from pure white, large pieces (rhombic crystals) to small fragments of a yellowish or reddish tint, in the same vein. The most common associates of barytes are the sulphides of the metals, especially lead sulphide, more rarely the sulphides of antimony, iron, or copper.

Preparation.—The mined crystals of barytes are sorted into greater or smaller pure white, reddish, or yellowish pieces, and separated from adhering gangue by aid of crutch-shaped iron tools. This operation is mostly done in suitable cemented reservoirs, provided with iron or wooden bottoms perforated with a number of holes. The single brands are then treated with a strong flush of water and at the same time the pieces are stirred with crutch-shaped iron bars so as to free them from the adhering stony matter, earthy or mineral bodies, &c. The washed pieces are then dried in the open air or in the plant described on p. 356, and, if necessary, again sorted, this time according to colour. The cleaned crystals are next coarsely crushed, or, if sufficiently fine, ground at once in edge-runners, and carried by means of conveyors to the mills. One or two grindings of the barytes powder being very rarely sufficient, the powder is generally milled three or four times. The powder from the first grinding is transported by conveyors to the second mill, from this to the third, and so on. After the final grinding the barytes powder is generally impalpable. The stones of the barytes mills must have a considerable diameter, and be of the best material, owing to the hardness of the barytes. The French stones are found to be the best, and are now exclusively used for this purpose.

Even the purest barytes crystals do not form a pure white powder when ground, but are of a yellowish or reddish shade. The manufacturer therefore "kills" the defective colour of the ground barytes by adding a certain quantity of ultramarine, generally during the grinding. This manipulation, although equivalent to intentional deception, is, however, not objected to by customers, probably because they are used to it.

A large number of brands of ground barytes are met with in the trade, according to the fineness or shade. The purest and finest brands are called *flowers of barytes,* while the more or less coloured ones, in view of their coarser textures, are denominated *barytes I.* or *II.—reddish* or *yellowish.* The product is sent out in barrels holding up to half a ton, or in bags containing 1 cwt.

Properties.—The trade product is a tasteless and inodorous, heavy white powder, of sp. gr. 3·9 to 4·53, according to purity. Barytes cannot be used alone as a colour on account of its exceedingly low covering power, even in the most finely ground state. It is quite insoluble in water and all dilute acids. Strong sulphuric acid dissolves about 3 per cent. (especially when heated), but on dilution with water the dissolved barytes is completely reprecipitated in an unaltered state. It is quite unchanged by calcination, but when heated with one-third of its own weight of carbon barytes parts with its oxygen, and is reduced to barium sulphide. Barytes is nearly always found admixed with smaller or greater quantities of calcium sulphate or carbonate, but seldom with barium carbonate or metallic sulphides. The inferior brands have a yellowish or reddish shade, due to the presence of ferric oxide, which can be removed by boiling with dilute acids and afterwards washing. In practice, however, although this method gives perfectly white brands from discoloured sorts without any technical difficulty, it is rarely used, if at all, principally because the price of barytes is very low and the natural impurities do not affect its use for most purposes. When calcined with alkali carbonates barytes is converted into barium carbonate:

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$

The same conversion is obtained, but less completely, by boiling it with solutions of alkali carbonates.

Use and Analysis.—The purer the whiteness and the finer the powder the greater the value and suitability of the barytes for most purposes. Barytes is used in manufacturing the various barium compounds, and all kinds are also extensively employed as a basis or adjunct in the preparation of mineral and lake pigments. As already mentioned, it is of no value as a painter's colour, since it has very little covering power when ground with water, and none at all with varnish. This property, however, makes it of special value as an adjunct to colours that cover well; and its absolute indifference to other chemical bodies is specially important. The addition of barytes to artificial mineral colours or to lake pigments is by no means to be classed as an adulteration, as the resulting colours are sold at a correspondingly low price, to the advantage of the buyer; and, again, most colours, especially the numerous lakes, would be of no practical use without this addition. For instance, the chromes, with their specially high covering power, and their mixed products, the chrome greens, could not be used as painter's colours without an addition of barytes, which facilitates distribution, brightens the shade, and favourably modifies the general workability of the paint. The same is the case with the lakes, the addition of white bodies (for poorer brands the natural barytes) increasing their brightness and suitability for use. The low covering power of barytes is here of special value, the shades of the lake pigments being brightened to the desired extent without their covering power being essentially changed, provided, of course, that no excessive quantity of barytes is used.

The fineness and the shade of the barytes suitable for colour manufacturing purposes depend, of course, on the properties and the commercial value of the colours in question. For very light and bright, or even white mineral colours, of course, only perfectly white barytes can be used, while for deeper, red or dark yellow grades, for instance, the yellowish or reddish brands of barytes can be employed. The same applies to the lakes, though it should be mentioned here that especially bright green lakes may often be unfavourably influenced even by very slightly red-tinged barytes.

The behaviour of barytes when ground with other colours in varnish is remarkable. Barytes requires only about 8 per cent. of varnish to attain the consistency of ordinary oil paints; hence colours that require large quantities of varnish (some, for instance, need 50 per cent. of their own weight) require a considerably smaller quantity when ground with barytes, their price being also considerably reduced. This favourable circumstance is largely utilised in practice, the more so because the low covering power of barytes has little effect on the good covering colours. Whilst in dry colours an excessive quantity of added barytes is easily revealed by their dulled appearance, this disadvantage is removed by the enriching effect of the varnish. Oil colours, therefore, are able to take such large quantities of barytes that here an adulteration with barytes might be spoken of. The absolute indifference of barium sulphate to all chemical reagents facilitates detection, and affords an effectual check.

The Analysis of Barytes.—Barytes should be tested for fineness of grinding, which can be easily done by spreading it out with a horn or steel palette knife, and especially for calcium sulphate or carbonate, barium carbonate, and ferric oxide. The tests will rarely be extended to added ultramarine or intentionally added metallic sulphides.

The content of *pure barium sulphate* is found by boiling a weighed sampl with hydrochloric acid, filtering, washing, drying, and weighing the residu after heating.

For the qualitative detection of the above-named adulterations a sampl of the filtrate is treated with barium chloride. A white precipitate show the presence of *gypsum* (calcium sulphate).

Another part of the filtrate is acidified with a few drops of pure hydrochloric acid and treated with one drop of a solution of potassium ferrocyanide A blue precipitate shows the presence of *ferric oxide.*

If on treating barytes with hydrochloric acid the mass froths up th presence of calcium or barium carbonate is indicated.

If a sample of the filtrate treated with sulphuric acid gives a white precipitate, *barium carbonate* (witherite) is present. If, however, in spite of distinctly observed frothing, no precipitate is obtained by an addition o sulphuric acid, a content of *calcium carbonate* is herewith indicated. A admixture of *ultramarine blue* can generally be detected by the naked ey (certainly with a magnifying glass), owing to the peculiar shade of th barytes. Ultramarine can be tested for by means of a strong solutio of alum or aluminium sulphate, a decided smell of sulphuretted hydrogen becoming apparent. If this smell is detected on adding dilut mineral acids instead of the said solutions, a (naturally admixed) *metallic sulphide* is present.

The quantitative analysis of the impurities named can, if required, be performed by the gravimetric method, impurities being easily separated from barytes on account of the absolute insolubility of barium sulphate.

Finally, a practical test for barytes may be given which enables a fairly reliable estimate to be formed of the kind of the crude barytes, colour, and (with a little practice) the impurities and the fineness of the grinding. This test is based on the behaviour of barytes towards turpentine. A small quantity of barytes is spread on a glass plate and moistened with a few drops of turpentine. If the barytes is absolutely pure a colourless, transparent mass is obtained, but if it contains even a small quantity of yellowish, reddish, or greyish brand of barytes that cannot be detected in the dry commercial article, the coloration shows up on adding the turpentine. Many persons in the trade have become so skilful in applying this simple test that they are able to dispense with actual analysis. By means of this simple test the fineness of grinding can also be distinctly observed.

Barium Carbonate (*Witherite*; $BaCO_3$)

Except for certain deposits in Germany, the only abundant sources of this mineral occur in England. The occurrence and method of mining are very similar to those of barytes; and the natural impurities, especially the metallic sulphides, are also the same in quality, but greater in quantity; but arsenic sulphide is sometimes also present. Barium carbonate occurs especially in crystals of the rhombic system, of less specific hardness, but of considerably higher specific gravity (sp. gr. 6·8 to 7·9) than barytes, and is seldom put on the market in such a fine powder as the latter. On account of its exceedingly low covering power, its poisonous properties, and dull tint, barium carbonate is of no use for colour-making. It serves as a raw material to manufacture various barium compounds, for which purpose its high solubility in hydrochloric acid (see p. 84) is specially favourable. The shade of the commercial powdered barium carbonate is rarely a pure white, but mostly strongly yellowish, greenish, or greyish. Witherite melts at a very high temperature without being decomposed.

b. THE NATIVE CALCIUM COMPOUNDS

Gypsum (*Calcium Sulphate, Lenzin, Annalin, Leichtspath*; $CaSO_4 + 2H_2O$)

Gypsum occurs in great abundance in many parts of the world, and forms (either alone or with anhydrous calcium sulphate) not merely important strata and rocks, but sometimes whole mountains. Two different principal conditions of the native mineral are known—the *true gypsum*, with two molecules of water of crystallisation, chiefly as crystals of the monoclinic system; and *anhydrous gypsum*, in rhombic crystals, the mineral being known as *anhydrite*.

In an impure, dense state gypsum forms abundant deposits of so-called *gypsum spar*; in a granular, crystalline state it is called *alabaster*; *satin spar* is a variety occurring as rod-like or fibrous masses; in large tabular pieces it constitutes *marienglass*. It also occurs combined with potassium or magnesium sulphates, in the rock-salt beds of Stassfurt, Berchtesgaden, Ischl, &c., and is then called *polyhalite*. Gypsum occurs in the purest state in the Muschelkalk, Keuper, and Zechstein formations, frequently as beds or stocks of a reddish or greyish tint; in a less pure state it is found in the lias. In Germany important deposits are found in Thuringia (Frankenhausen, Koenigsee), Franconia, and Würtemberg; and at Osterode (Harz) it forms whole mountains. Pure white ground gypsum has different names in commerce, according to the fineness of the powder, and is called *Leichtspath, Lenzin, Federweiss* in Germany. *Annaline* is calcined ground gypsum.

Properties.—Gypsum contains two molecules of water of crystallisation, and has therefore the formula $CaSO_4 + 2H_2O$. It occurs in large monoclinic crystals, sometimes twinned and dovetailed. The crystals are sometimes very perfect, but have a low degree of hardness, and are generally somewhat flexible.

Gypsum is soluble with difficulty in water, and less soluble in hot water than in cold. The maximum solubility is reached at about 35° C. 1000 parts of water dissolve at zero C. not quite 2 parts of gypsum, but 2·8 parts at 14° C. If ammonium chloride is present gypsum dissolves more readily. If crystallised gypsum be heated for a certain time to 90° C. it loses about 15 per cent. of water, and the rest on raising the temperature to 170° C., the gypsum then becoming perfectly anhydrous.* If a saturated solution of gypsum be heated in a closed glass to 130° to 150° C., crystals of $2CaSO_4 + H_2O$ are deposited, but readily take up water again below 130° C. Boiler fur consists for the most part of this compound. Gypsum from which all, or nearly all, the water has been expelled is called *burned* or *calcined gypsum*, but when moistened reabsorbs the two molecules of water expelled by the heat, and gradually sets to a solid mass. This behaviour of the burned gypsum is utilised for moulding and casting purposes, and for making mortar. Gypsum heated above 200° C. is said to have been *killed*, being no longer able to take up again its water of crystallisation, or, at any rate, will not set hard with water until a long time has elapsed. The specific gravity of gypsum is 2·33.

Preparation.—Whereas formerly gypsum was prepared for various industrial purposes in a most complicated, irrational way, different brands of gypsum are now ground in the same manner as barytes. Gypsum being about half the cost of barytes, and of considerably lower specific gravity, the diurnal output requires to be much greater in order to secure a profit. The greater softness of the gypsum, of course, facilitates the working, the repeated grinding required in the preparation of barytes being mostly superfluous in this case. For many technical purposes—*e.g.*, mixing with ultramarine—very fine grinding is not at all necessary. The grinding is therefore easier, and requires, in spite of the greater daily output, a smaller plant and less complicated, expensive machinery than for most other natural mineral colours. As a rule, the raw material can be sufficiently worked in edge-runner mills, the use of heavy, powerful crushers being dispensed with. The subsequent fine grinding, exclusively effected by edge-runners, is also more simple. The aw material being soft and loose, the millstones need not be set very close, nd the mill therefore runs more easily and better, with less consumption of ower. The former practice of wet grinding was rendered unprofitable by he cost of drying the humid mass, and as the product was no finer or better n colour, has now been entirely discarded. Gypsum works are now fitted p entirely for dry grinding, the sifting process having also been abandoned, wing partly to the difficulty and partly to its being unnecessary; therefore ypsum is now sifted only when specially ordered to be so treated.

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* According to *le Chatelier*, gypsum is converted at 120° to 130° C. into a compound $2CaSO_4 + H_2O$, and becomes perfectly anhydrous at 160° to 170° C.

The manufacture of calcined gypsum was also carried on at one time in a simple and sometimes unsuitable manner, the lumps of gypsum being generally interspersed with the fuel, so that a superficial reduction of the calcium sulphate to calcium sulphide ($CaSO_4 + 4C = CaS + 4C$) occurred, thereby rendering it useless for many purposes.

Gypsum is calcined in *gypsum kilns*. The simple kiln, still often used, consists of four strong walls covered with a flat roof containing several flues. The fireplaces are placed on opposite sides. The larger lumps of the raw material are built up in arches in the kiln, to serve as channels for the hot gases, and topped with the finer portions. A suitably strong wood fire is maintained during the whole process, and the openings for charging and discharging the kiln are tightly stopped.

The kiln recommended by *Scanegatty* for calcining gypsum is very similar in construction, charging, and working to that for ultramarine illustrated in Fig. 59. The inside of the kiln is divided at about 16 ins. to 20 ins. above the bottom into two chambers of unequal size by a flat partition provided with discharging flues. The gypsum is charged into the upper and larger chamber by the aid of a door at the one side and through a hole in the partition above (in the place of the chimney shown in Fig. 59). The lower, smaller chamber communicates direct with the fireplace, which is under the kiln, and is arranged for burning coke or coal. The up-draught carries the flame first into the lower chamber, and then through the numerous openings into the calcining chamber, which it traverses in all directions the spent gases then escaping into the open air by the flue at the top. Steam is formed in considerable quantity at the beginning of the process, and escapes into the air through a number of vertical flues in the partition.

In the *shaft furnace* proposed by *Riva* the air for combustion is forced by a blower into sets of heating chambers below the stove, arranged side by side and superimposed, and thence through flues and openings in the side by a fan. At the lower end of the kiln is an inclined pipe for discharging the burned gypsum.*

Various other forms of gypsum kilns are used; for instance, those with movable trucks; but a description of these would occupy too much space here.

The calcined gypsum is ground in mills like the raw material to a powder of varying fineness, according to the purpose in view. For many purposes, however, the gypsum obtained by the method described above is unsuitable. Finer brands are manufactured by heating ground, pure white gypsum (containing water) to 170° C. in large iron pans provided with stirrers, the water escaping and producing considerable agitation in the powder. In this method of preparation no further grinding is required.

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* For description see Dr. F. Fischer, *Chemical Technology*, 1889.

Use.—On account of its low covering power and want of stability, gypsum cannot be considered as a real colour. It plays a certain part, however, in colour making as an adjunct for producing cheap brands. A great number of artificial mineral colours as well as the earth colours and lake pigments are considerably cheapened by an addition of gypsum without suffering any special deterioration—for instance, the chrome yellows, the various brands of ultramarine blue, Bremen blue, copper-arsenic greens, some chrome greens, &c., the addition of gypsum to which has already been mentioned under their respective headings. Many earth colours, however, especially the red and yellow ferric oxide colours, the brown manganese oxide, even the various brands of lampblack pigments, are mixed with sometimes considerable quantities of gypsum, according to their covering power and other properties, to regulate their commercial value. In this case there is no real adulteration, the colours being so low in price that no one of experience imagines them to be pure. Besides, the manufacturers take care in their own interest to avoid any addition of gypsum where it would adversely affect the use of the colours—for instance, in lithographic printing, wall-paper printing, and fancy paper making.

The gypsum used for colour purposes is generally the powder obtained by grinding the natural gypsum, more rarely burned gypsum that has been reconverted into the hydrated form by treatment with water, followed by drying and grinding. The shade of gypsum should be a pure white, yellowish, reddish, or greyish, according to the purpose in view. All these shades of gypsum can be formed in colour works, though the pure white brands are preferable. With a few exceptions, the finest possible grinding is essential to the use of gypsum as an adjunct, especially when the mixtures are prepared by precipitating the colour materials directly on to gypsum from their solutions. If coarse-ground gypsum were used in such cases the colours would be fuller in shade, but would exhibit a fatal tendency to yield white streaks, on account of the coarse particles, when spread out with the palette knife.

Examination.—Except the test for colour and fineness, no analysis is made of gypsum for colour making purposes.

Though the other technical uses of raw and burned gypsum do not come within the scope of this work, the most important, however, may be briefly mentioned here.

Crude gypsum is sometimes used as a *building material*, but is gradually dissolved by rain. The dense, fine-grained *alabaster* is used by sculptors. Ground raw gypsum serves as a manure, especially for meadows and clover. Burnt gypsum is specially used for plaster casts of all kinds (plaster of Paris), stucco, cement, mortar, &c. In using dehydrated gypsum for casting and reproduction purposes a thin paste of 1 part burnt gypsum with 2 to 2·5 parts water is used. On the formation of the resulting gypsum crystals ($CaSO_4 + 2H_2O$) the rest of the water is mechanically occluded, but evaporates for the most part when the materials are dried, these latter then assuming the well-known porous appearance. A well-burnt gypsum usually sets hard in one to two minutes, and becomes slightly warm. Generally some kind of glue is added to delay the setting process ("binding"), and also to impart greater hardness and a marble-like appearance to the gypsum. This kind of gypsum is generally used for architectural ornaments, decorations,

&c., various effects being produced by the addition of colours, such as indigo, certain earth colours, colcothar, lampblacks, &c. To produce *alum-gypsum* (plâtre aluné, French stucco, marble cement) plaster articles are dipped in a warm solution of 600 parts of alum in 3000 of water for fifteen to thirty minutes, and treated with a solution of alum when cold, the result being a crystalline superficial layer. This method has been simplified by treating powdered gypsum with a solution of alum and recalcining it after drying. This alum-gypsum sets hard as easily as ordinary gypsum when ground, but the plaster has to be mixed with alum solution.

Parian cement is gypsum hardened with borax.

Calcium Carbonate ($CaCO_3$)

This compound occurs in a pure state as the minerals *aragonite* and *calc-spar*, usually met with in well-formed crystals belonging to two different systems.

Calc-spar, or *calcite*, crystallises in the hexagonal system, the fundamental forms being the rhombohedral, the scalenohedral, or the hexagonal prism, rarely the pyramidal. The number of the different forms and combinations is very great, exceeding two hundred. *Calc-spar* is found abundantly in the Spessart and the Odenwald, near Heidelberg, the Upper Palatinate, near Rettwitz, in Sweden at Marmorbrücket and Motala, and in smaller quantities in Silesia and many other places. A variety of calc-spar is found in Iceland, near Rödefiord, the so-called doubly refracting *Iceland spar*, forming perfectly transparent and generally colourless rhombohedra, which are used for optical purposes. The term calc-spar is a collective name, comprising all the crystallised or distinctly individualised varieties of calcium carbonate, whilst the also numerous and most important forms of crystalline, fibrous, shell-like, or granular to dense texture are called *marble*, *fibrous lime*, *slate spar*, *limestone*, &c. When the mountain streams containing calcium bicarbonate in solution, percolate through the roofs of natural caverns the gradual evaporation of the carbonic acid and the water precipitates neutral calcium carbonate, and the so-called *stalactites*, sometimes of very marvellous shapes, are then formed. *Calcareous tuff* and *pearl sinter* are formed in a similar manner.

Chalk and *mountain milk* are earthy, amorphous or crypto crystalline, easily pulverisable varieties of calcium carbonate.

Aragonite crystallises in the rhombic system, but also forms parallel and radial fibrous aggregations. To the latter forms belong especially the so-called *pisolites*. *Iron bloom* and *sprudelstein* (from calcareous springs) form encrustations and stalactitic deposits. Of all these calcium carbonate minerals only *chalk*, ordinary *limestone*, and *calc-spar* are used for colour manufacturing purposes.

1. *Chalk, Whiting, Paris White, English White, Spanish White (Kreide, Blanc de Meudon, de Paris, de Troyes, d'Orléans; Blanc Minéral, Craie)*

This substance, sold under all these names, is one of the most important components of the cretaceous formation, which is of very extensive occurrence in many parts of the world. In Europe it is found in abundant deposits on the English coasts, on the Danish islands, in Sweden, at Rügen, Usedom, and Wollin, in Champagne, and in many other places. Sometimes it occurs as a thick limestone (Pläner limestone, or chalk), or it forms rocky masses containing irregular nodules of flint with enclosed silicified shells, and of iron pyrites. The crude chalk is generally contaminated with a variable quantity of clay, iron oxide, or manganese oxide, and sometimes of organic matter. It is generally obtained by quarrying.

Preparation.—The preparation of the crude chalk for various purposes differs according to the climate. In wet, northern countries the raw product is stacked in the open air, to be weathered by atmospheric influences. The stacks are exposed to rain and dry winds alternately, and especially to frost, so that the initially hard stone is crumbled to a powder that readily mixes to a paste with water, which afterwards is levigated in the usual way. In France and Spain, where this cheap method of preparation is precluded, or only possible at certain times of the year, on account of the insufficient rainfall, the crude product is suitably crushed and then levigated. Since the carrying out of this process depends on the properties (especially the hardness and purity) of the mineral, the methods, as well as the appliances and machines, used differ considerably, so that a detailed description would be difficult, and we shall therefore deal merely with generalities.

In some cases the chalk, after being rendered friable by weathering, is freed from coarse impurities, such as flints, lumps of pyrites, &c., and afterwards ground in large wet mills (for machinery see Fig. 9). In others the harder masses of chalk are first crushed in mills like those illustrated in Figs. 39 and 40, to prepare it for levigation. The circumstance that the coarse impurities are reduced as well is very little drawback, their higher specific gravity causing them to settle down quickly during levigation and to readily separate from the suspended chalk. For this reason any crushing machine will do for chalk, provided it is of ample capacity, not liable to be choked up, and will deliver the chalk in a finely powdered state suitable for levigation. If wet mills or machines of similar construction are used the first grinding may be rough, the desired fineness being obtained in the final grinding.

The levigation process varies very much in different places. Local circumstances and the size of the works naturally determine the size of the plant used. Levigation factories are mostly equipped with a very simple and efficient levigator, consisting of a reservoir 13 to 20 ft. in diameter, round or polygonal (twelve- or sixteen-sided) in shape, and 40 to 60 ins. in depth, and sunk in the ground. This reservoir is lined with brick and cemented; or, more simply, an enclosure is made with thin, strong deal planks, backed with puddled clay. A strong post is driven into the ground exactly in the middle of the reservoir, to serve as a firm support for a cross-arm stirrer extending right to the edges of the tank. Each arm (generally four) of the stirrer is fitted with teeth reaching to within about 1½ in. of the bottom of the reservoir. The teeth are vertical, and set about 4 to 6 ins. apart, and are fastened together by laths so as to form a number of triangular points turned towards the bottom of the reservoir. They may be either of wood or iron; in which latter case they will be of round section, tapered and somewhat bent at one end, the other (straight) end being bolted, about 1½ to 2 ins. apart, to the rake arms. With this arrangement no cross-stays are needed. The four rake arms are mounted on a strong iron ring so as to form a cross with square arms. The central post is provided at the head with a recess in which this ring fits exactly, so that the cross is suspended and able to move in all directions, the rake teeth passing over the whole bottom of the reservoir. If the teeth are made of iron rods these latter are bent at the top in the direction of movement. The machine is driven by steam, water power, or by draught animals. This tank communicates direct by channels with a number of settling tanks, situated on both sides of the plant. The settling tanks are mostly rectangular pits, lined on the sides and bottom with laths, to keep the whiting out of direct contact with the soil. These tanks are placed close together, being separated only by a partition wall, so that the liquid mass can be transferred to all by means of a common gutter. The whiting is usually allowed to dry in these tanks, and the feed channel is therefore provided with a sluice for each, so that when tank one is full the second, third, &c., can be charged, thus making the operation continuous. By the time the last pit is full the contents of the first one should be dry, or at least sufficiently stiff to enable the mass to be spread on boards to finish drying. This circumstance must be borne in mind in determining the number of settling tanks to be used.

The method of working with such a plant is briefly as follows: When the levigating tank is filled with water about three parts full the rake is set in motion and the weathered or crushed chalk is fed in by degrees. After a sufficient stirring has been given, the discharging gutter to the settling tanks is opened, and a suitable continuous stream of water is run into the levigating tank. The steady, gentle flow carries off the finer particles of whiting into the settling tanks, where they settle down; the coarse parts, however, remain in the levigating tank, where they are worked over again along with a fresh charge.

Sometimes the settling tanks are in connection, not with the levigating tanks, but with large crushers or stamps (Fig. 80), provided with a suitable levigator. Since all the other apparatus used for preparing whiting are generally based upon the same principle, there is no need for any further description.

Drawing chalk, cut into long quadrangular pieces, for writing on blackboards, can be made (according to Gentele) in the following way: Finely levigated chalk is mixed with milk of lime and slowly dried in large blocks, the added lime being gradually converted to calcium carbonate and binding the whole together, so that it can be sawn. Another way is to form a mixture of chalk paste with burnt gypsum, the mass also in this case hardening so that it can be sawn, whilst at the same time it becomes suitable for writing with. Levigated chalk forms when dry a soft, friable mass, which for commercial purposes has to be suitably reground. The special disintegrator mills used now for this purpose not only give a very fine product, but are also able to turn out large quantities in a short time.

Large quantities of unlevigated chalk ("powdered chalk") are put on the market in a finely divided state, and with good covering power. This article is prepared by grinding very pure lump chalk in disintegrator mills and sifting the product in the dry state. This brand is as good as the ordinary chalk for many purposes. A very pure and white chalk of this kind is found in Russia near Bjielgorod (Weissstadt).

Properties and Use.—Chalk is the amorphous modification of native calcium carbonate, and consists of calcareous chambers (coccoliths) of foraminifera and the *débris* and fragments of the shells of numerous other organisms (molluscs and crustacea). The fragments are soft, have an earthy or conchoidal fracture, and a specific gravity of 2·2 to 2·5. Levigated chalk should be free from hard, foreign bodies, have a brilliant white colour, and mark easily. The natural impurities, which cannot be removed by the purely mechanical method of preparation, consist generally of small quantities of clay, iron and manganese oxides, organic bodies, traces of other calcium compounds, &c. Chalk is easily decomposed by hydrochloric and nitric acids, acetic acid, and even by many salts—*e.g.*, aluminium sulphate, alum, &c.—carbonic acid (CO_2) being liberated, and the corresponding soluble or insoluble calcium salts formed. When heated, chalk loses carbonic acid and is changed into calcium oxide. It is absolutely insoluble in pure water, but dissolves to some extent in water containing carbonic acid, calcium bicarbonate being formed.

Commercial whiting varies greatly in quality, according to the origin, method and care of preparation, &c. Whereas the former chiefly determines the purity of colour, the method of preparation, of course, mainly influences the fineness and covering power. Whiting has good covering power as a water colour, though with oil (varnish) it does not cover at all. Chalk paint made with oil dries but very slowly, if at all, and always has a dirty yellowish look. For this reason it is absurd to add chalk or whiting as an adjunct to paint, as is often done. When mixed with size, both levigated and crude whiting, if ground fine enough, will give a smooth, uniform paint of good covering power, even when mixed with mineral or earth colours of inferior covering power. For this reason whiting is largely used in the manufacture of wall-papers and ordinary distempers. A mixture of *levigated* whiting with a strong solution of glue to form a stiff paste makes a very good priming for indoor painting—*e.g.*, woodwork, cheap furniture, &c.—but is unsuitable for outdoor use. If the glue be replaced by mineral oil or talc, or both together, or pure boiled linseed oil, a kind of cement is obtained which is useful for many purposes, especially as glazier's putty.

Whiting is rarely used as an adjunct to artificial dry mineral or earth colours, and merely plays a subordinate part in the manufacture of a few lake pigments.

A proper analysis of whiting is rarely needed in the colour trade, and therefore need not be described. Whiting can be easily detected in dry colour mixtures by the effervescence produced on treating the article with dilute hydrochloric acid, provided the colour is not itself a carbonate. In this latter case ordinary qualitative tests must be made.

2. *Limestone, Quick and Slaked Lime*

Occurrence.—Ordinary limestones occur, similarly to chalk, in massive beds which have a slightly crystalline character, especially in the *Muschelkalk* and *Keuper formations*. The limestone of the Muschelkalk is the more crystalline, and is the predominant constituent of the formation, which owes its name to the abundance of the fossil shells found in it. The overlying and more recent *Jurassic formation* consists mainly of limestone (the *Jura* or *oolitic limestone*), which is less crystalline in character, and has fossils representing a different fauna. In the *Keuper* and *Liassic formations* it is less pure, of a more marly composition, has fewer fossils, and is subordinate to the predominating beds of gypsum and sandstone.

Preparation.—Ordinary limestone is used exclusively for making quicklime, which when slaked with water forms the principal ingredient of mortar. For this purpose the limestone is calcined, whereby it loses carbonic acid and is converted into calcium oxide, CaO, quicklime. The latter combines with water (heat being liberated) to form calcium hydroxide, $Ca(OH)_2$, which is used with sand as a mortar. By taking up carbonic acid from the air it is gradually reconverted into calcium carbonate and becomes hard again. The calcining or "burning" process of the limestone may be explained by the following equation: $CaCO_3 = CaO + CO_2$; and that of the so-called slaking by the equation $CaO + H_2O = Ca(OH)_2$. The hardening of the calcium hydroxide may, however, be explained by the following equation: $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$.

Limestone is burned in large kilns of various shapes. The limestone is mixed with the fuel (wood, coal), or else the heat is applied from lateral fireplaces, the flame entering the interior of the kiln, or three special fireplaces are arranged round the furnace, the flame entering from these into the kiln. The burnt lime is discharged through openings at the bottom of the kiln, fresh quantities of limestone being fed in at the top. About 50 per cent. of the weight of the limestone is lost in the burning. The product cannot be kept for any long time, and is therefore mostly slaked at once, and the resulting pasty mass stocked in pits. The admission of carbonic acid is prevented by the supernatant lime-water, which soon becomes covered with a skin of calcium carbonate.

Limestone containing silica, clay, or magnesia cannot be slaked, or only with difficulty, the lime being *killed* If the temperature be too high alumina and silica form compounds with the lime, which do not give a stiff paste with water. If the lime contains magnesia it is not slaked to a fatty, plastic mass, but forms a granular paste. Hence the classification into *fat* and *thin* lime. The former only is suitable for mortar.

For chemical purposes quicklime is prepared by calcining pure calcium carbonate, marble or calc spar. The expulsion of carbon dioxide is imperfect unless the lime be maintained in an atmosphere of inert gas. For this purpose carbon monoxide (CO), or sometimes atmospheric air only, is now generally used. In the former case the result is obtained by charging the kiln with alternating layers of lime and coal (brown coal, wood coal). The burning coal reduces the carbon dioxide to carbon monoxide, and is entirely consumed: $CaCO_3 + C = CaO + 2CO$.

Quicklime has the property of chemically fixing about one-third its own weight of water, the temperature rising considerably, and the mass crumbling to a fine white powder. This *slaking* process is carried out in various ways, according to the use for which slaked lime is intended. If a fine dry powder be desired the quicklime is sprinkled with just one-third its own weight of water. This water is quickly absorbed by and combined with the very porous lime, the temperature rising quickly (to 150° C.). The mass crumbles to a dusty powder, the surplus water escaping as a cloud of steam. If, on the other hand, the lime be sprinkled with more than its own weight of water it forms with the surplus water a thin paste, which quickly sets to a stiff mass. During storage in the pits the *lime paste* thickens, the undecomposed particles contained in the freshly slaked lime being gradually slaked by the action of the water.

When an excess of water is used a thin white pulp is formed, *milk of lime,* from which the undissolved hydroxide settles down on standing, whilst the top liquor is a solution of calcium hydroxide in water, in the trade called *lime-water.* This saturated solution of lime contains 1 part of calcium oxide, CaO, in 760 parts of water, and is therefore very weak.

Properties and Use.—Calcium oxide, or *quicklime,* is a white to greyish, earthy or porous, infusible mass, with a strongly alkaline taste. The dust has a corrosive action on the skin and lungs. When allowed to stand in the air quicklime absorbs water and carbonic acid, and forms a soft, loose powder. This action must be prevented, being really a conversion into calcium carbonate, which is then unslakable. Calcium oxide does not decompose in the blowpipe flame.

In the dry state *calcium hydroxide* is a soft, white powder with an alkaline reaction. It has a caustic taste, and is decomposed when heated into calcium oxide and water. It is very sparingly soluble in water, 1000 parts of water dissolving only about 1 part calcium hydroxide, cold water dissolving rather more than hot, so that lime-water prepared at the ordinary temperature becomes cloudy when boiled. Dry calcium hydroxide readily absorbs carbon dioxide from the air, and is converted into calcium carbonate. It must therefore be kept in the form of a very stiff paste, in which state it presents a smaller absorbent surface than the soft powder.

The aqueous solution of calcium hydroxide, *lime-water,* has an alkaline reaction and taste. It absorbs carbon dioxide from the air, the dissolved hydroxide being precipitated as insoluble white calcium carbonate. For this reason lime-water must always be kept in tightly closed bottles.

Quick or slaked lime is largely used in various ways, and is a very important commercial article. As already mentioned, it is used to manufacture caustic soda and caustic potash from the corresponding alkali carbonates. Slaked lime plays an important part in the manufacture of acetic acid from wood, also in manufacturing oxalic acid, alum and aluminium sulphate, bleaching powder, sugar from beetroot, ammonia from sal ammoniac, for preparing skins in tanning, for treating cotton in bleaching, &c. Its chief employment, however, is for making mortar.

As milk of lime, slaked lime is largely used for coating plaster and stone walls. The calcium hydroxide forming a thin film on the wall, is very loosely adherent at first, and can easily be removed by the fingers, but changes by-and-by into calcium carbonate by taking up water and carbon dioxide, and becomes quite hard. This so-called "binding" of the lime can be furthered by the addition of finely ground curd, casein, skim milk, &c. The casein contained in the milk and curd forms a caseate with the calcium hydroxide, and when dry becomes so hard that walls covered with it are impervious to moisture, rain, &c. The important manufacture of *weather-proof paints for outside work* is based on this property of the casein-lime compound. These pigments are obtained *in a pasty condition* when ordinary cheese curd is treated with about one-third of its own weight of commercial ammonia. The resulting mass is mixed thoroughly with about the same quantity of powdered calcium hydroxide, an equal quantity of chalk, and a little of the earth colours ultramarine blue or ultramarine green, and finally ground in a suitable hopper mill (Fig. 9). If the mixture becomes too stiff, it is thinned down with water to a workable condition. The product is sold in hermetically closed tins, in which it keeps well for a long time. For use the pasty mass is thinned down with water if necessary. The ammonia contained in the preparation evaporates on drying.

Dry weather-proof painter's colours are made by treating definite quantities of powdered slaked lime with chalk, mineral, and earth colours, and intimately mixed with 10 to 20 per cent. of powdered casein (blood casein) in the usual way. For use the product is generally simply mixed with water and applied immediately. The dry pigment has, however, one inconvenience; the calcium hydroxide after a certain time becomes converted into calcium carbonate, the subsequent hardening of the coating of paint being considerably retarded, if not prevented entirely. A brand of casein has recently been placed on the market under the name "Lactarin," which, when mixed with whiting only, and without calcium hydroxide, gives a weatherproof paint possessing all the properties desired.

The use of slaked lime in colour-making, especially in producing the mineral colours, has already been mentioned, and its use for lake pigments will be referred to in connection with these latter.

3. *Calc-spar* (*Paris White*)

This term comprises those natural calcium carbonates which are principally found in primary limestones as coarsely cleaving crystals, and in a very pure state. When finely powdered, they are equal, if not superior, to whiting, the colour particularly being very often much whiter. Calc-spar is ground in the same way as barytes (*q.v.*), but, being softer, does not require grinding so often. Powdered calc-spar, or *Paris white*, as it is sometimes called, is of a greater specific gravity than whiting, but if sufficiently fine has the same covering power when used as a distemper. As an oil colour the covering power, however, like whiting, is only very low.

Paris white is scarcely ever used in colour making, one exception being as an adjunct to chrome green, which will stand a high proportion without deterioration of shade. The mixing is always made in the dry state in an edge-runner or a ball mill.

Powdered calc-spar when heated yields a very pure white lime, and is therefore very often used in the chemical industry. The resulting calcium hydroxide is used in the manufacture of lake colours as a precipitating agent for alum or aluminium sulphate, these latter being decomposed into aluminium hydroxide and calcium sulphate.

Calcium Phosphate (*Bone Earth*)

Neutral calcium phosphate occurs native as hexagonal crystals of *apatite* which also contains variable quantities of calcium fluoride and calcium chloride. Under the names of *phosphorite* and *osteolite* it is found in the amorphous, earthy, or crypto crystalline state, the latter especially nea Limburg and Amberg.

The above-named double compounds of native calcium phosphate cannot be used for colour-making, not being in a suitable state, nor can pure neutral calcium phosphate be cheaply obtained therefrom in a suitable form for serving as a base for mineral or lake colours. The only suitable product is that obtained by calcining or chemically treating bones, for which reason the process will now be briefly described, though it really does not fall within the scope of this section.

Bone earth is manufactured by two methods, viz.:

1. By calcining bones (after removing the grease) in the open air; or
2. By precipitating a hydrochloric acid solution of the inorganic constituents of bone with caustic potash.

The *calcining* is generally effected in kilns which, even in large works, are very similar to lime-kilns (*q.v.*) in form and dimensions. A layer of wood is placed on the bottom of the kiln, and over this the bones, the wood being then ignited and the fire kept up. The perfectly calcined (white) bones are removed through an opening, and fresh bones are put in. The very malodorous gases are led off through a strong sheet-iron cowl into the chimney, which must have a good draught. It is preferable to burn the gases as completely as possible, thus saving fuel. 100 parts of fresh bones give 50 to 55 parts of calcined bones.*

The product forms irregular white lumps of such slight hardness that they can easily be ground to a soft, fine white powder in edge-runners, ball mills, &c.

The manufacture of calcium phosphate by *treating degreased bones with hydrochloric acid* is part of the bone-glue manufacturing process, and is generally performed in the following way:

Boiled bones in crates hung on rods in wooden tanks are treated with hydrochloric acid of sp. gr. 1·05. The bones remain in these crates until perfectly soft and all the inorganic matter is dissolved out. The residue is then worked up for glue, whilst the repeatedly used and saturated hydrochloric acid solutions are collected in a large wooden tank, where they are freed from iron (originating in the hydrochloric acid), and the phosphoric acid is precipitated as neutral calcium phosphate by the aid of quicklime and calcium carbonate. The precipitate generally contains 18 to 20 per cent. of phosphoric acid, but with proper care it can be obtained in a very pure state. In this case sufficient very pure milk of lime is added to the hydrochloric acid solution of calcium phosphate to neutralise the acid. The calcium phosphate is completely precipitated as a white mass, while the readily soluble calcium chloride, formed at the same time, remains dissolved. After being washed and freed from the adhering calcium chloride, calcium phosphate forms a very white powder, of much purer composition than that obtained by calcination. It is sometimes used as a base for manufacturing lake colours.

Properties.—Tricalcium phosphate, $Ca_3(PO_4)_2$, is not decomposed when calcined alone. It is insoluble in pure water, but somewhat soluble in water containing carbonic acid, common salt, ammonia salts, or certain organic bodies. It dissolves in hydrochloric acid, nitric acid, and sulphuric acid, being converted into acid calcium phosphate (monocalcium phosphate), $CaH(PO_4)$. Tricalcium phosphate is artificially obtained by precipitating an ammoniacal solution of calcium chloride with sodium phosphate. It forms a transparent jelly like precipitate, which turns to a white earthy powder when dried.

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* F. Fischer, *Manual of Chemical Technology*.

c. THE NATIVE SILICATES

Magnesium Silicate

Occurrence.—This occurs native in various very important minerals, the best known of which are:

(*a*) *Olivine*, Mg_2SiO_4 or $2MgO.SiO_2$, or *chrysolite* (rhombic crystals), the magnesia being partly replaced in some specimens by ferrous oxide.

(*b*) *Serpentine*, $3MgO.2SiO_2$ with $2–3H_2O$ or $Mg_3Si_2O_7+(2–3)H_2O$ (also rhombic crystals).

(*c*) *Talc, soapstone, or steatite*, $Mg_3H_2Si_4O_{12}$ or $3MgO.4SiO_2.H_2O$, hexagonal rhombic plates. A variety of this compound is *meerschaum*, $2MgO.3SiO_2+(2 \text{ or } 4)$ molecules of H_2O.

Magnesium silicate is also found as magnesium double silicates, of which the most important are *augite* and *amphibole*, which are essentially calcium magnesium silicates. A variety of amphibole is the technically important substance *asbestos* (calcium magnesium silicates of varying composition).

Talc (*Steatite, Talcum, French Chalk*)

Besides the augites, which will be fully described with the green earth colours, talc—*i.e.*, powdered steatite—is the only native magnesium silicate used for colour-making. It is not a true colour in the proper sense of the word, but is frequently prepared in the manufacture of earth colours Talc comes on the market as a powder, chiefly from Bohemia and Trieste, though of late the work of talc-grinding has sometimes been undertaken as a subordinate operation by some German makers of earth colours. Owing to its low degree of hardness (= 1), talc-grinding is a very simple process, and is mostly done in large wet mills, the material being rarely ground in the dry state. The finely ground talc is separated from the top liquor in settling tanks or pits by decantation, and the stiff paste is dried on the drying-boards already fully described, the mass being stirred at intervals. Subsequent grinding or sifting of the dry talc is generally unnecessary, the dried lumps crumbling to a very fine powder under the slightest pressure.

Properties and Use.—As a mineral (soapstone) talc forms a white to greenish white, soft body of foliated or scaly structure. It is sometimes transparent in thin layers and of nacreous lustre, so as to be often confounded with mica, from which, however, it differs by its inferior transparency and elasticity, as also by a soft, greasy feeling. When ground it forms an impalpable, soft powder of a greenish white tinge. It shares, though in a much smaller degree, the property of clay for fixing basic coal-tar colours without any precipitating agent, but is not used for this purpose, the resulting lakes being very deficient in brightness and covering power.

Talc is used for polishing marble and gypsum articles, for manufacturing tailor's chalk, pastel colours, face powder, &c.

Aluminium Silicates (*White Clay, China Clay, White Bole, Porcelain Earth, Kaolin, Pipeclay*)

Alumina forms with silica (alone or in association with other metallic oxides) various compounds which play an important part in Nature. The various kinds of clay are produced by gradual decomposition of *felspar*, which with quartz and mica forms an important component of granitic, gneissic, or porphyritic rocks. In the weathering of *potash felspar* (*orthoclase*, $K_2Al_2Si_6O_{16}$) potassium silicate is for the most part dissolved by the water and removed, a smaller portion, however, being decomposed by carbonic acid, with liberation of silica, while the potassium carbonate is dissolved by water; aluminium silicate is left, which, with the silica, forms a solid residue. The gradual decomposition of all felspathic rocks takes place in this way, the clay becoming mixed with sand, lime, and other substances, loam (coloured yellow by iron) being formed. When the residual clays are found on their original site they are termed *primary clay*. If, however, these bodies have been transported and changed by the influence of water (the coarse, heavier foreign admixtures being extracted, and the true clay left in a more concentrated and finely divided state), the product is known as a *secondary clay*. This kind generally forms dense plastic masses when mixed with water.

The primary clays can be regarded as mixtures of quartz, undecomposed felspar residue, and true clay. They vary greatly in character with regard to appearance, shade, and other properties, which difference can be easily explained by the variation in the proportion of the principal components—silica and alumina—a good deal also depending on the admixtures present. These in the poorer clays are chiefly sand, magnesium and calcium carbonate, barium compounds, iron oxide, sulphur compounds, and organic residues. The sandy impurities are partly true quartz sandstone, or *silica*, soluble in caustic potash, and partly fragments of undecomposed minerals.

The purest clay, *porcelain earth*, or *kaolin* (china clay), is formed by the weathering of very pure felspar, and is chiefly found in secondary deposits. The best known are at Halle and Meissen, near Aschaffenburg, in Bavaria, in some parts of the Palatinate, Hungary, Moravia, France, and England (Devonshire).

Clays capable of giving a stiff paste with water are called *fat* or *plastic clays*. They consist exclusively of mixtures of pure aluminium silicate and silica. The presence of foreign bodies, especially lime and sand, amorphous earths, &c., reduces the plasticity of the clay more or less, according to the quantity of the admixtures; this kind is called *meager clay* (non-plastic). *Marls* are clays rich in calcium carbonate. Most primary clays are non-plastic, but can be rendered plastic by eliminating the impurities by a suitable levigating process.

The *preparation* of the various kinds of clay differs according to their nature. The mostly non-plastic clays used for colour-making are prepared by a single (rarely repeated) dry grinding in stone mills, or even in edge-runners, to a suitable white powder, needing no further sifting, which would be very difficult. The preparation of china clay consists in a more or less careful levigation, but as it belongs more to the pottery industry it need not be gone into here.

In view of the special properties and the abundant quantities of native clays, a special preparation for colour-making is rarely needed, it being easy to get clays so pure that a simple stirring up with water and then sifting the pulp through a fine sieve (to remove sand, small stones, &c.) is quite sufficient for colour-manufacturing purposes.

Properties and Use.—With regard to the practical use for colours, the shade and to a certain degree the plasticity (capacity of binding) of clay form the decisive factors.

Pure clay is white, other shades being the result of certain definite impurities, chiefly ferric oxide, ferrous oxide, and more particularly organic matter. Coloured clays, of course, are only suitable for certain purposes; but the manufacture of very light and bright colours requires a pure white clay, or one only slightly tinted yellow, green, or bluish grey, whilst the darker kinds are suitable for manufacturing dark pigments. Plastic clays are not often used for colours, on account of the trouble they give in working, whether in the wet or dry state. As already mentioned, non-plastic clays are generally preferred, the more so because they usually furnish much purer and brighter shades. Moreover, the capacity of fixing basic coal-tar colours—the chief point in question—is usually no greater than is possessed by the non-plastic clays.

Apart from possibly pure whiteness, a clay suitable for colour purposes must be capable of rapid dispersive suspension in water. The non-plastic paste, after being coloured with organic colouring matters, must be easy to wash, filter, press, and grind. After drying the lumps must be of a rather soft nature, whereby much trouble on grinding is avoided. The numberless varieties of *marl* are very largely used for colour purposes, on account of their possession of these qualities. These bodies are found in so many places that nearly every colour-maker has an available supply, and as the nomenclature is generally local* it is quite impossible to give particulars about the character and properties of all. Colour-makers must form their own opinion of the raw material offered them by means of tests.

Powdered clay, such as china clay, white bole, &c., is now rarely added to dry pigments, for reasons connected with their properties—*e.g.*, the difficulty experienced in distributing the clay, this entailing severe grinding to obtain uniformity of shade in the dry mixture, an operation that of course dims the brilliancy; also the greasy nature of the clay, slight degrees of which are readily detected if the dry mixture is spread out. The chief reason, however, is that clays do not dry, or only very slowly, when ground with oil—a defect imparted in a very considerable degree to all mineral colours that are mixed with clay.

An addition of clay, however, is advantageous to all mineral and lake pigments intended solely for distemper paints or washes—*e.g.*, in the wall and fancy paper industries, paints for toys, &c.—since the covering and printing properties are considerably improved, and the easy equalising of the colour much facilitated. The kind of clays used, however, must be most carefully selected, many of the plastic clays (especially china clay) not always being suitable for this purpose.

An important matter is the content of ferric hydroxide or ferric oxide either mechanically mixed or chemically combined, in various kinds of clay If such a clay contains much ferric hydroxide it is yellow-coloured, and belongs then to the important class of argillaceous *ochres.* If the iron, however, be admixed as an oxide, the substances have a reddish to deep red tint, and are then called *red bole* or *ruddle.* This is found, like ochre, in considerable quantities.

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* The so-called "Walkerde," &c., of the German colour trade.

These clays, which are largely used for painter's colours, will be fully described in connection with the yellow and red earth colours later on.

Pure clay is white in tone, mostly of low specific gravity, soft, pulverulent, and unctuous to the touch. When breathed on it emits the so-called clayey smell. With water it forms a paste of varying thickness, which shrinks in drying, sometimes into hard lumps, which are difficult to break. When cautiously heated to redness pure clay parts with its water, shrinks, and forms a hard, porous mass, *burnt clay.* Hydrochloric acid and nitric acid have no action on pure clay, but it is decomposed by sulphuric acid, assisted by heat, and by boiling or calcining with caustic alkalies. Heated to very high temperature by itself, pure clay softens, but does not melt.

The uses of the various kinds of clay are well known. The purest and whitest variety, china clay, serves as a material for porcelain manufacture. The less pure kinds are used for making stoneware, faience, and ordinary earthenware.

II.—YELLOW EARTH COLOURS

THE NATIVE COMPOUNDS OF IRON

Ochre (*Yellow Earth, Chamois, Chinese Yellow, &c.*)

Ochres vary greatly in form and composition, and occur native in very large quantities. They may generally be regarded as decomposition products of the various kinds of ferruginous felspar and similar minerals. Many ochres must be considered clays, on account of their high content of aluminium silicate, and among them those containing much lime, especially the various kinds of marl. The colour varies from a pure yellow to dull orange and brownish red, according to the content of iron oxides. These may occur as hydroxide alone, or mixed with variable quantities of ferric oxide, ferro-ferric oxide, manganese oxide, or basic ferrous sulphate. If there is also a more or less considerable quantity of calcium carbonate and organic bodies, or both together, a number of greatly varying intermediate shades are obtained. The shade of pure ochres, which, of course, alone can be used for colour-making, depends, therefore, on the content of ferric oxide and hydroxide, and therefore two classes of ochres can be distinguished:

1. *Yellow ochres,* mixtures of clay or calcium carbonate with ferric hydroxide.
2. *Red ochres,* containing, in addition to these components, varying quantities of red ferric oxide.

1. *Yellow Ochre*

Occurrence.—Yellow ochres occur of various colours and degrees of purity, as deposits in cavities in stratified rocks in many localities, chiefly at Ocker, near Goslar, Elbingerode, Tilkerode, Jena, Ransbach, in the Westerwald district, near Wunsiedel, Siegen, and in France. Also in Thuringia, near Saalfeld, Grossbreitenbach, Koenigsee, &c., yellow ochres, sometimes of great brilliancy, are found. In fact, ochres of a more or less bright appearance occur in nearly all countries, and are won from their deposits by mining or digging.

Properties.—Yellow ochres meet with the largest sale of any, and are known under various names. The purer and specially bright kinds are sometimes called *oxide yellow, golden ochre, satinobre*, &c., those of a greenish tint being sometimes termed *bronze ochre, bronze brown*, &c. As already mentioned, the yellow tone is the consequence of a varying content of ferric hydroxide, and is purer in inverse ratio to the amount of other hydroxides, especially brown manganese hydroxide. The larger the content of pure ferric hydroxide the brighter and stronger the tone, and at the same time other properties, such as covering power, softness, &c., are considerably increased in intensity. The already mentioned manganese hydroxide, which is always found with iron compounds, has very little influence if present only in small quantity, but if more abundant turns the colour to a more brownish shade on account of its own brown colour, the value of the product being considerably reduced. The brownish kinds are more suitable than the pure yellow ochres for manufacturing the popular olive-green shades, by mixing the ochres with yellow or green artificial mineral colours, though their use for this purpose is small relatively to their native abundance. An excessive proportion of ferric hydroxide is sometimes indicated by a decided brownness of tone; but the commercial value of the product is not affected, since this kind of earth colour can easily be utilised for colour purposes. With suitable white substances, like barytes, chalk, artificial barytes, lithopone, &c., or of yellow mineral colours (chromes, &c.), pretty shades can be obtained. The covering power of these mixed pigments is generally not unduly lowered by ingredients of inferior covering power like barytes or chalk, the ochres rich in ferric hydroxide having in general a greater covering power than the pure yellow ochres.

On account of their content of clay, nearly all ochres are difficult to mix with other pigments in the dry state, especially when the ochre is specifically lighter and forms the greater part of the mixture. In the trade, however, various brands of mixed ochres are met with, the best known being the so-called *chrome ochres*, distinguished by their very bright colour, high covering power, and better drying properties than the ordinary yellow ochres. As already indicated by their name, chrome ochres consist principally of a mixture of pure ochre with suitable shades of chrome. They are put on the market in shades ranging from nearly pure bright yellow to the deepest brownish-orange tint, and are prepared by grinding pure ochre with chemically pure or baryted chromes in definite proportions, first in edge-runners and afterwards in mills.* Sulphur-, lemon-, or orange-shaded chromes can be used, according to the desired shade of the mixed colour; but it may be mentioned that with most brands of ochres chemically pure chromes are more difficult to mix than those containing barytes.

An important property of all brands of ochre is their changeability at high temperature. As already mentioned in describing the calcining process, the colouring principle—viz., ferric hydroxide—is decomposed when heated to redness, parting with its water of hydration and changing into red ferric oxide. Since other components—chiefly aluminium silicate and calcium carbonate—are also modified by the heat, an entire change of the original ochre is produced, the specific gravity and covering power being also considerably heightened. The chemical and physical processes which take place in calcining ochres have been fully described when dealing with the chemical treatment of earth colours. Something may, however, be said about the change in external appearance.

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* Experience proves that the direct precipitation of lead chromate upon a base of ochre in the form of a thin milk gives brighter shades. [TRANSLATOR.]

Though in the calcining process the greater part of the organic bodies, always present in impure (viz., clayey) ochres and the cause of their greenish tinge, are oxidised, the burnt ochres are never of a pure red colour, but are always more or less brown. As already explained, this coloration is due to the presence of manganese hydroxide, but is less perceptible in the crude ochre. By the heating process, however, the brownish manganese hydroxide is changed into the more decided red-brown manganese oxide. The *brightness* of the shade after the heating process depends exclusively on the composition, and cannot be regulated either by the duration of the process or by the temperature applied—a fact explained by the nature of the calcination products, viz., chiefly ferric oxide, which above a certain temperature is no longer subject to change. As a rule, bright yellow ochres acquire when calcined a relatively deeper reddish tone, and reciprocally the less bright kinds furnish correspondingly duller reds. The only advantage of an addition of common salt, as sometimes recommended in the heating process, is—if of any practical value at all—to regulate the temperature. Some kinds of ochre become greatly discoloured (grey-brown) when overheated for a considerable time, especially those containing much calcium carbonate. These kinds, however, never furnish agreeable reddish shades even with the greatest care, and should therefore not be used for calcining.

Apart from the shade, the *covering power* and the specific gravity of most kinds of ochre are changed to a considerable degree by calcination. Whilst the covering power is generally considerably raised, the volume of the heated product is reduced and the density increased, the one being generally a natural consequence of the other, or *vice versâ*. This behaviour, however, varies with the kind of ochre, and an exception is afforded by ochres rich in clay, the volume diminishing considerably without there being any appreciable increase in the covering power. The reason for this is to be sought in the shrinkage of clay at high temperatures, a change that is very seldom combined with any noteworthy rise of covering power (with oil). Hence only ochres mainly consisting of pure ferric hydroxide or rich in organic matter will shrink when heated, and at the same time will exhibit a considerably improved covering power, due to the resulting ferric oxide.

For these reasons no distinct rules and directions can be given for the choice of ochres suitable for being heated, and even a thorough knowledge and experience of the trade will be insufficient so long as the character of the ochre in question has not been proved by suitable trials.

The *drying property* in varnish is also considerably improved by calcination. This fact is based upon the peculiar properties of the clay, the loss of the water of hydration, and the destruction of the organic bodies, or, in other words, upon the considerably harder nature of the calcined product, whereby for paints a much smaller quantity of varnish is required. Sometimes, however, varnish paints from burnt ochres dry very slowly, and are easily and entirely washed away by rain in the open air. This serious defect is mostly shown by ochres which contain (in the crude state) considerable quantities of calcium carbonate. In the calcining process the carbonate is converted into quicklime, which forms a soluble soap with the varnish, whereby the thin coating is quickly decomposed. (Of course, the quicklime could be reconverted into calcium carbonate by prolonged standing.)

2. *Red Ochres*

Occurrence and Properties.—Compared with the yellow ochres, the red kinds are of subordinate importance. With regard to shade, they come between the yellow ferric hydroxides and the pure ferric oxide colours and they can be prepared, as already mentioned, by calcining the first-named, though in this case they are, of course, much dearer than those obtained from natural deposits. For this reason the native red ochres are preferred to the artificial kinds for cheap paints.

Red ochres of rather inferior quality occur in moderate quantities in a great many places. Good kinds are found in the Roten Berg (red mountain), near Saalfeld, in Hesse-Nassau, Bohemia, England, France, &c., always as tough (often clayey) masses of low tenacity and earthy fracture.

With regard to their general properties, they differ but very little from the yellow or brownish ochres—in fact, merely in point of shade, the tone being a dull yellowish or brownish red of small intensity, according to their composition. Their reddish tinge, as already explained, is based upon the very varying content of ferric oxide, mostly accompanied by considerable quantities of clay and calcium carbonate, with a small content of iron and manganese hydroxides. Red ochres are therefore changed very little by calcination, only the alumina being influenced, apart from the conversion of ferric hydroxide into oxide. Hence no improvement of tone or any other property can be expected from calcination of this kind of ochres. With few exceptions, therefore, the natural red ochres need no other preparation after calcination. They are only ground after calcination, and seldom levigated. Red ochres are put on the market under various names, according to origin, occurrence, or tone. Paints made with red ochres generally dry slowly, but are mostly durable. The natural red ochres are only used for wall-paper making and other industries on a small scale, at least as true colours, but more extensively for shading and mixing purposes, together with other ochres and red ferric oxide colours.

Siennas (*Terra di Siena, Italian Earth, Terre Ombre, Mahogany Brown, Cashew Lake*)

Under these names a number of earthy colours belonging to the ochres both as regards composition and appearance are put on the market. Siennas are mostly found in the Harz and in Tuscany. They are dug out of the earth in the form of dark brown to yellowish brown, sometimes very hard lumps, with lustrous conchoidal fracture, and furnish a bright yellow to brownish yellow powder on grinding. The tone of this powder is much brighter and fuller than any other ochre, and affords an easy means of recognition. Sienna is the purest native form of ferric hydroxide known, and is very similar in composition and appearance to the artificial product. A large proportion of clay is seldom present, though impurities, such as sand, quartz, and organic matter, are found.

On account of their composition, siennas are greatly changed by calcination both in form and (chiefly) colour, the latter becoming brown, reddish, orange to dark red, according to their purity. Gentele found in many brands considerable quantities of sulphuric acid, besides ferric hydroxide. The varying changes of tone are perhaps due to this fact, the calcination products of the sulphuric acid probably inducing the formation of differently coloured stages of oxidation of ferric oxide.

Whilst the other raw ochres are of medium covering power, which is considerably improved by calcination, siennas have but a low covering power in either condition, approximating more to the transparent or glaze colours, and, in fact, are exclusively used as such. Their property of darkening considerably when ground in varnish is also shared by the mixtures into which they enter. Raw sienna requires about one-third of its own weight of varnish to make a paint of ordinary consistence, but less when calcined (about 25 per cent.). The paints dry slowly when laid on thickly, but more quickly as thin coatings. Ground sienna is largely used for litho- and typographic printing, and as an artist's colour, either alone or mixed with organic lake pigments, the sienna serving as a base, on which the organic colouring matters are precipitated from the solution. A lake of this kind is the *mahogany lake* (cashew lake), well known in lithographic and letterpress printing. This lake, as well as raw and burnt sienna, is put on the market in cubes, drops, corrugated tablets, and as a powder.

The preparation of ochres differs according to their physical character. Many kinds, for instance, occur in such a pure state that when dried a simple grinding under edge-runners or in a ball mill, &c., is quite sufficient to furnish a fine, usable powder. Some, however, are of such a clayey nature that grinding is quite impossible, even in the absence of sand or other bodies. The only way to grind these to a sufficiently fine powder is in admixture with others of a less clayey nature. Most raw ochres, however, are levigated in the usual manner near the place of their deposit, and sold for colour-manufacturing purposes in the shape of soft lumps.

A good idea of the levigation of native ochre as practised near Saalfeld, in Thuringia, is given below, the particulars being taken from an article in the *Deutsche Industriezeitung* (1879, p. 324).

The crude earth, freed from all non-colouring elements, is left for a certain time in the open air, especially during winter, for the purpose of simplifying the generally difficult process of comminution. Sometimes the earth has to be exposed for several years before it can be subjected to purely mechanical treatment (according to the degree of hardness) in the works. The refractory portions (a small percentage of the whole) are treated in a stamping mill, levigated by a continual stream of water, and allowed to settle, or else the coarsely crushed earth is ground in wet mills and afterwards levigated. The bulk of the earth colours, however, is levigated without any preparatory treatment.

The levigation is effected in a cylinder 60 ins. high and 30 to 40 ins. in diameter, in the centre of which is a rotary iron shaft provided with arms and teeth, that stir the charge of colour and water at the rate of 25 to 30 revolutions per minute. The thin sludge runs away through a pipe at the side, and the coarse sediment is removed through an opening as near the bottom as possible. The usual settling devices are employed. The drying of the sludge is a difficult operation, the amount of water being about the same as that of the dry substance even after standing for some days, and still more in the case of very clayey ochres. Filter presses are generally used for treating the kinds that settle very slowly, centrifugal separators being seldom used owing to their low capacity. The fairly stiff drained paste is laid on drying-boards about 4 ft. in length and 10 ins. broad (Fig. 30), and is dried on racks in the open air. A colour works of medium size producing about 250 tons of levigated ochre requires about 60 to 70 racks, each carrying 100 drying-boards. The dried, irregularly formed lumps rarely suit the requirements of customers, the moist powder form being in greater request; and since in this state the material looks better and is easier to pack, besides mixing better with lighter or darker brands, the interests of the manufacturer and consumer are identical. Edge-runners, as well as ordinary mills, are used for grinding the levigated ochres, but for grading and sifting the machines shown in Fig. 63 are employed. With the aid of a continuous elevator these machines will sift 1 to 2 tons of dry material daily, according to the character of the goods.

Besides the above described ochres there are other *ochre like colours* in the trade, which may be called *sludge ochres,* being by-products of alum and vitriol manufacture, and not true earth colours in the proper sense of the word. The so-called *alum sludge* is the sediment obtained in most alum works on evaporating the crude lyes. It takes the form of a crystalline, granular, yellow precipitate, very similar in composition to the basic ferric sulphate thrown down by ferrous sulphate solution on prolonged standing in the air (see Part III., *Iron Compounds*). The sediment from crude alum liquor, however, is generally contaminated with a considerable quantity of gypsum, thrown down concurrently during the concentration of the liquor. When calcined, dried alum sludge loses first the chemically combined water, becomes dark red in colour, and afterwards parts with all the sulphuric acid present, the residue consisting of red ferric oxide.

The so-called *vitriol ochre* is obtained as a bright yellow-coloured sediment or precipitate by lixiviating the spent iron pyrites used in manufacturing ferrous sulphate in large tanks; and it is also formed in considerable quantities in the liquors collecting in the workings and old galleries in pyrites mines. These yellow sludgy precipitates are very similar to ochres, but on account of their want of covering power have to be put through a suitable treatment. In the crude state they contain, in addition to ferric hydroxide, considerable quantities (up to 16 per cent.) of sulphuric acid, and are therefore of about the same composition as raw siennas. On calcination they are converted into ferric oxide, more than one-third of the weight being lost in the process.

In localities where these ochres are very abundant they are stirred up with water and led into special suitable pits, the water gradually soaking into the earth, and the ochre left behind as a stiff paste.

III.—RED EARTH COLOURS

Besides the natural vermilion, now entirely displaced by the artificial product, the number of native red minerals suitable for pigments, and therefore red earth colours in the proper sense of the word, is very small, being confined to the red clays containing more or less ferric oxide, the sole type of which is the so-called *purple red, Venetian* or *Indian red, bole, oxide red, raddle* or *red chalk*. *Red iron-stone*, an iron ore of a blood-red colour, cannot be considered a true pigment, as it possesses no advantages in comparison with the much cheaper and easily obtainable artificial red iron pigments. The same remark applies to *micaceous iron*, which is much more easily ground to a fine powder, but in this state has a peculiar unctuous violet lustre prejudicial to its practical application.

The red natural mineral colours, which are therefore exclusively ferric oxide compounds of varying purity, can be classified into:

(*a*) Ready-formed natural pigments—Indian red (bole), or raddle; and

(*b*) Pigments obtained by the chemical treatment of natural iron ores—iron minium (English red, oxide red, caput mortuum, &c.).

a. Indian Red (*Bole, Purple or Venetian Red, Raddle, Red Chalk*)

The ordinary Indian red, bole or raddle, is a clay containing a large quantity of ferric oxide, and therefore of a light to dark red tone. It is found in layers and deposits of considerable magnitude, especially in the "Bunter" sandstone, and to a smaller extent in the lias. The best-known deposits of Indian red are near Wunsiedel, in Bavaria, Striegau (Silesia), Scheibenberg (Saxony), near Göttingen, on the Rhine, near Carlsbad, &c. The so-called *Armenian bole*, or *Lemnos earth*, is found as more or less hard, tough, brown-red masses of greasy lustre in Armenia, Lemnos, Malta, Hungary, Saxony, Silesia, &c. The principal impurity consists of variable quantities of sand or large quartz fragments, more rarely organic matter or differently coloured clays.

Besides its colour, Indian red has all the properties of ordinary clay: it forms with water a plastic paste, it becomes much harder, without changing colour, on calcination, but with loss of the mechanically or chemically fixed water, and is then in a less suitable condition for being treated with water, &c.

On account of its ready distribution in water it can be freed from mechanical impurities without any difficulty by levigation, though this is seldom done. It is generally put on the market after a simple drying in the same shape as it is found, sometimes in masses weighing over a hundred weight. It is chiefly used as a water colour for painting walls and wood; when mixed with white substances (lime, gypsum, &c.) it gives pretty pink shades (peach-blossom red). Bright brick red to dark red, especially pure kinds, are used for manufacturing red pencils, or when sawn into suitable pieces are used for writing (red chalk, raddle). Crude Indian red cannot be used as an oi colour, but in the calcined state it forms a mass which, under the name *ston red*, is sometimes used for varnish paints.

b. Ferric Oxide Colours Obtained by Calcination

The red ferric oxide colours described under this heading are partly metallurgical products or are obtained from the chemical industry, mostly as by-products. In part they are also specially manufactured in colour works by the calcination of certain widely distributed and abundant natural iron ores. The iron ores mostly used for this purpose are:

1. *Red hæmatite*, Fe_2O_3, a crude earthy variety of native ferric oxide, is found in lodes and beds in primary rocks, and is known by various names, according to its physical character (*iron ochre, blood-stone, iron-stone*, &c.). In admixture with silica it forms the so-called *clay-iron stone*, with lime compounds *minette*. *Iron glance* is crystallised ferric oxide. All red iron ores have a more or less characteristic red tone, and are nearly all suitable for colour-making.

2. *Limonite, bog ore*, &c., are found in brown or black pasty or bulbous nodules or cakes in the alluvium of the North German plain, in Bavaria, &c. It consists principally of ferric hydroxide and ferrous hydroxide, with varying quantities of manganese oxide, phosphoric acid, organic bodies, sand, &c.

3. *Brown hæmatite*, $H_2Fe_2O_4$ to $H_6Fe_2O_6$, is formed by the action of air and water containing carbonic acid on spathic iron ore or ferrous carbonate, $FeCO_3$.

Iron Red (*Oxide Red, Iron Minium, Eisenmennige*)

The pigments found in the trade under this name contain 82 to 88 per cent. of pure ferric oxide, and are obtained from one of the foregoing iron ores by sorting out the most suitable pieces, and strongly calcining them in a reverberatory furnace very similar to that described under the heading dealing with the chemical treatment of the earth colours, until the water of hydration is expelled and the cooled ore has acquired a bluish-red tinge. The temperature and duration of the process depend on the nature and composition of the ore, and must be ascertained beforehand by experiment. As a rule, the very hard, dense ores require a higher temperature and longer calcination than soft limonite, for instance, to expel the water of hydration. The shape and size of the lumps to be calcined also have a not unimportant influence.

The effect of calcination differs according to the physical character of the ore. Whereas sometimes an ore will retain its strength and structure, only the shade and specific gravity being changed, at another time the same ore will become more porous and softer, so as to fall to powder, or at least change to a condition considerably facilitating comminution. Others, again, that are naturally softer, like bog iron ore, become hard and dry, sometimes vitreous, and therefore difficult to grind. Hence no distinct rules with regard to the regulation of the calcining process can be given, and it is therefore easy to understand that one and the same ore cannot always be treated in exactly the same way. The further treatment of the calcined products depends, of course, on their character, due to the foregoing calcining process, but as a rule the good products are immediately separated from the inferior ones, and each class is further treated by itself.

Whilst the softer products can be ground direct, one or more times, in ordinary mills (with French stones), the harder and hardest materials must be first treated in edge-runners, stamp mills, or other similar machines, and afterwards thoroughly levigated. For this purpose a stamp mill with levigation plant or wet mills can be used, and the levigating process is exactly the same as that already repeatedly described. The very finely divided red mass obtained from the levigating tanks is generally placed, without any filtration, in the form of a thick sludge, on the drying boards frequently mentioned (see *Ultramarine*), and dried until the water content has been reduced to 2 to 3 per cent. at the utmost. In this state the lumps of ferric oxide are soft, easily rubbed to powder by the hands, and without any difficulty readily ground in a pulveriser to a fine powder— the oxide red of the trade.

In many works the reverse way of manufacturing oxide red is adopted. The crude ores are first treated in edge-runners, balance mills, pulverisers, &c., according to their hardness, then levigated, and after being dried are calcined in iron cylinders. The result is the same in both methods, the only question being which is the cheaper.

At present considerable quantities of iron reds from the spent pyrites ("burnt ore") obtained, for instance, in great quantities in the manufacture of sulphuric acid, are met with in the trade. Pyrites, FeS_2, when roasted in the air, is oxidised to ferric oxide and gaseous sulphur dioxide:

$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2.$$

The gas is passed into leaden chambers, whilst the ferric oxide is left behind in irregular lumps of varying hardness and weight, and of bluish or brownish red colour, mixed with small quantities of pure red particles. These iron residues were formerly wasted, and therefore considerable quantities accumulated in the neighbourhood of sulphuric acid works. These heaps underwent a process of weathering, the atmospheric influences oxidising the highly complex compounds of iron and sulphur present, ferrous sulphate being formed and gradually leached by the rain, leaving a pure and in part a very brightly red coloured ferric oxide behind. Although only the outer layers were decomposed in this way, this natural decomposition revealed new and extensive sources at the disposal of the colour-maker, and the method is to-day employed to some extent for manufacturing iron reds. At first an attempt was made to imitate the result of the natural decomposition process—viz., the removal of the sulphur—by repeated calcination in a reverberatory furnace. The dull, dark, bluish or brownish tint of the spent pyrites was believed to be due to the presence of sulphur, but neither the colour nor the physical character of the product was improved, even by the aid of powerful oxidising agents. The price of oxide red being now very low, the fresh or already wasted spent pyrites is usually subjected to a mechanical treatment only, calcination being omitted. The mass is levigated, or more often ground in the dry state in edge-runners, balance mills, or pulverisers. In a few cases where it is thought that the raw material has not been properly burned it is calcined either before or after levigation. The liberation of large quantities of sulphur dioxide during calcination shows the correctness of the assumption.

Properties and Use.—The oxide red of the trade is a fine, bluish red to brownish red powder of good covering power, and resistant to all external influences. A coating of oxide red paint is a perfect protection against rust, a property upon which is based the extensive use of this pigment for painting ironwork. Oxide red is entirely free from acid, and is rarely adulterated, owing to its low price, which of course furthers the extensive use as pigment. It is with great difficulty soluble in nitric acid and sulphuric acid, but dissolves more readily in hydrochloric acid, though only after prolonged boiling. Varnish paints made with oxide red dry slowly as a rule, but are very hard and preserve wood very well, especially when tar is added. Oxide red paint is very durable, lasting for many years without suffering any appreciable change.

Oxide reds mix perfectly well with artificial and natural mineral colours of similar appearance, the mixtures furnishing a great number of very agreeable and permanent paints. Used alone as an oil colour, the red generally darkens a little in time.

English Red from Artificial Sources (*Prussian Red, Colcothar, Venetian Red, Italian Red*)

The red iron oxide colours brought into the trade under these names are at least equally important with the above described oxide red. They vary in shade from the lightest scarlet to the darkest bluish red, being then very similar to the oxide red already mentioned.

The chief raw materials are *alum* or *vitriol sludge* (vitriol ochre) and *green vitriol* (ferrous sulphate).

The Manufacture of Colcothar from Alum Sludge.—This is a by-product of alum works, and considerable quantities of iron oxide are obtained in this way. For this purpose sludge deposited from the alum liquors is prepared by a levigation process and then classified. This operation is generally done in the ordinary levigating tanks, provided with stirring arrangements. The coarse parts removed by the first levigation are added to fresh portions or repeatedly levigated until no more fine particles settle down. The pasty sediment is then dried on boards until it feels damp, but will not smear when rubbed between the fingers. From this prepared alum sludge colcothar is obtained by calcination in a furnace containing several muffles placed one above another. The furnace gases pass over the mass laid on the bottom of the muffle, and calcine it, the gases then escaping along with the acid vapours through an opening in the arch and into the chimney common to all the muffles. The main object of the calcining process is, of course, to obtain a uniformly burnt product. The muffles must therefore be made as short as possible, since in long muffles the gases cool down too much as they get further away from the furnace, and the product in such a case is, of course, unequally coloured. This defect is remedied by the use of suitably constructed reverberatory furnaces, which are now often used for this purpose. They are very similar to that shown in Fig. 73, except that the bed is quite level and that a large opening (mostly in direct connection with the chimney by means of a flue) is provided to enable the voluminous acid vapours to escape.

The manufacture of colcothar by calcining vitriol sludge is performed in the way just described, and the construction of the furnaces is the same.

After being levigated and dried, the alum mud, as well as the yellow-red sediment (vitriol sludge) formed by concentrating solutions of ferrous sulphate, are calcined in large iron pans until the water of hydration and the sulphuric acid are expelled. By this method, however, only the yellowish and not the pure red shades of colcothar are obtained, so that the method cannot be recommended.

The true so-called *caput mortuum* is formed, as before mentioned (p. 334), as a by-product in the manufacture of Nordhausen (fuming) sulphuric acid, but is also obtained direct by calcining copperas (ferrous sulphate), the escaping sulphur trioxide being passed in a suitable manner over metallic iron, thus producing a further quantity of copperas. If obtained in the manufacture of fuming sulphuric acid (p. 334), caput mortuum is differently coloured according to the heat to which it has been exposed. The product from the lower retorts of the furnace is always darker coloured than that from the upper retorts. Before proceeding to work it up into crude caput mortuum the furnace residue must therefore be sorted into at least two shades, viz., light and dark. When a sufficient quantity is collected each kind is treated separately under heavy edge-runners, and afterwards ground to a fine powder in balance mills (with French stones). It is then recalcined with an addition of common salt, the temperature being cautiously regulated. The treatment in this recalcination differs according to the desired shade, while the quantity of common salt used and the duration of the calcining process play a very important part. As a rule, the shade of the calcined product is a darker blue-red (violet) the higher the temperature, the larger the quantity of common salt, and the greater the duration of the calcination. The yellowish shades of colcothar require an addition ot 2 per cent. of common salt and heating for about an hour; medium, somewhat brownish kinds 4 per cent. of common salt and three to four hours' heating; the deepest and more violet kinds, however, need up to 6 per cent. of common salt and at least six to seven hours' calcination, the speed at which the temperature rises being also an important matter. Again, the rate of cooling the calcined product, with or without admission of air, also naturally influences the shade of the colour.

The furnaces used for the recalcination of caput mortuum are very similar to those used for manufacturing fuming sulphuric acid. The calcining is done in long clay pipes, like the oil retorts, mounted in five rows, one above the other, twelve pipes in each row. The furnace gases impinge on the whole surface of these pipes, which are charged and emptied from the outside. In this arrangement the temperature is rather difficult to regulate, the contents of the pipes nearest the furnace being fully calcined, while in the superior series the action has only just begun. The calcination therefore requires to be controlled during the whole process. Little has been published about the methods of manufacturing caput mortuum by the direct calcination of copperas, and the utilisation of the resulting sulphur trioxide. The authors therefore do not know whether the process described by *Leech* and *Neal* in the *Chemiker-Zeitung* (1879, No. 14, p. 166) is actually in use or not. A short description is, however, appended. Copperas is calcined in a furnace heated by several fires (according to the size), containing a certain number of flat clay pans for holding the copperas. In the roof of the furnace is placed a small chamber, which communicates with two iron pipes provided with throttle valves. One of these valves leads into the chimney, the other, however, into a second chamber lined with lead, and communicating by means of an iron pipe with a chamber built of fire brick, and charged to a depth of about 40 ins. with iron filings or other scrap iron. Above the chamber is a water tank, with a double perforated bottom. An iron pipe leads from this chamber to the chimney. When the furnace is charged the valve communicating with the leaden chamber is opened as soon as the sulphuric acid begins to be decomposed by the heightened temperature, whilst at the same time the pipe leading into the chimney is closed. The volatile decomposition products enter the leaden chamber, filled with water to a depth of a few inches to absorb the trioxide, whilst sulphur dioxide passes into the chamber which is partly filled with iron filings. By the aid of a slowly trickling flow of water, the sulphur dioxide combines with iron to form copperas, which collects in vessels on the bottom. The other vapours, which cannot be utilised, escape into the chimney. As after the decomposition in the furnace is finished, the calcining has to be continued, the valve leading into the leaden chamber is closed, and direct communication re-established between the furnace and the chimney. The liquor in the leaden chamber is then concentrated in the ordinary way, and the crystallised copperas used for fresh charges.

The ferric oxide obtained by one of the methods described above is rarely used as pigment without some further treatment. It generally needs repeated grinding, and for some purposes must also be more or less carefully levigated.

Properties and Use.—The iron oxide pigments grouped under the trade name of colcothar vary considerably in shade, and are the cheapest red painter's colours at present known. They have a very high covering power, and unless they contain a certain quantity of acid, in consequence of careless treatment, are very permanent. Colcothar can be used for coating lime and cement, as well as mixed with these two materials in any desired proportion, without suffering any change. The varnish paints dry relatively quickly, are generally very hard, and sometimes resist atmospheric influences for many years. This, however, applies mostly to painting on wood or non-metallic objects, the sulphuric acid present in consequence of the method of manufacture having, even in the smallest quantity, a corrosive action on metal and the vehicle, so that the paint perishes in a comparatively short time. For this reason the various brands of colcothar cannot be recommended as anti-corrosive paints, since they facilitate rather than prevent the formation of rust.

Colcothar is sparingly soluble in mineral acids, but only on boiling, though more readily so than iron red from iron ores. It can be mixed with artificial and natural mineral colours in any desired proportion, and is consequently used in very large quantities. Intentional adulterations are rare, and the presence of sometimes considerable quantities of barytes, gypsum, and even chalk in many brands is generally accompanied by a corresponding reduction in price. In addition to the manufacture of wall papers, colcothar, owing to its indifference toward alkalies, is also largely used for weather-proof outdoor paints, and for paints with or upon lime.

IV.—GREEN EARTH COLOURS

GREEN EARTH

Bohemian or Veronese Earth (*Tyrolean Green, Cyprian Green, Seladon Green, Stone Green*).

The minerals called "green earth" in the colour trade occur native as augites, which vary considerably in composition and are widely distributed. The *true green earth*, however, so long used as a green painter's colour, occurs only in a few places in Central Europe. These colours can rarely, if ever, be taken as true green pigments, at least considered alone, their shade being mostly rather grey than green, and it is only when they are spread over white earth colours, or, better, red ones, that they look distinctly greenish. Verona, Tyrolean, and Bohemian green earth, however, resemble a real green, especially with oil, the tone being bluish or yellowish, according to the purity of the product, but always of only low brilliancy and colouring power. They are found in a specially bright and pure state in Monte Baldo, near Verona, Cypria, in Bohemia, and more or less impure in the Tyrol, in the Harz, at Zwickau (Saxony), on the Rhine, &c, mostly in thin beds and pockets, sometimes as a lining to amygdaloids.

Green earth in the crude state forms a wet, clayey, tough to earthy mass of very varying tone and purity. The pieces and lumps coming from the pits must therefore be sorted according to the deeper or lighter shade, and more particularly freed from adhering yellow ochreous substances. This work is always performed in the pits. The purer and purest lumps are of a pale bluish-green shade, with a strong greyish cast, and only become somewhat brighter after the subsequent preparation. With regard to shade, Bohemian, Cyprian, and Verona earths are the brightest, the first-named especially being of a pure green tone, though Cyprian earth is rather yellowish green and Veronese earth always bluish green in colour. The Tyrolean brands mostly look duller than the above-named, but sometimes resemble the Veronese product.

Green earth is now very seldom used as a true painter's colour, the modern colour trade having brighter green pigments available, some of them as permanent as green earth. In admixture with clay it is sometimes used as so-called *stone green*, and with other materials, such as lime, chalk, barytes, gypsum, for weather-proof outdoor paints. In a very pure state green earth is somewhat used as a varnish colour, and also by artists. On the other hand, the native *augites* are now very largely used as a base for the highly important *lime colours*. Augite has the formula

$$m[(MgFe)O,(AlFe)_2O_3,SiO_2] + n[(MgFe)O,CaO,2SiO_2],$$

m and n being variable proportions. It consists, therefore, of a magnesium aluminium oxide and ferrous silicate, and is therefore a kind of clay, the greenish tint being due to the ferrous oxide. The use of augites in modern lime colours is based on their capacity for fixing basic coal-tar colours to a certain extent without the aid of precipitants, and so firmly that the resulting colours are quite proof against the alkaline action of quicklime. The coal-tar colours mostly used for this purpose are auramine, brilliant and malachite green, methyl violet, magenta, &c., which when used alone or in mixtures furnish a rich collection of fairly permanent bright lime colours. The various brands of augite, or so-called green earth, however, differ in their properties when treated with coal-tar colour solutions, the quantity absorbed and shade produced varying with the colour of the earth and the content of silica and other components present.

Both the augites and true green earth are usually prepared by dry grinding in the usual way, more rarely (and only for finer brands) by levigation. In the first case, the dried raw products from the pits being generally rather soft, a simple grinding in ordinary mills (even pulverisers for specially fine brands) is mostly quite sufficient. If the raw material, however, be hard or very lumpy a preliminary rough grinding under edge-runners is necessary.

Ground green earth is a light, impalpable (rarely coarse) powder, unctuous to the touch, and more or less glossy when spread out by the aid of a palette knife.

Calcined green earth was at one time largely used as a painter's colour. It is obtained by the calcination of the raw earth as a dull brownish red powder, but is now rarely employed.

Mountain green, the *malachite* of the mineralogist, basic copper carbonate, also belongs to the natural green mineral colours. Being, however, rarely used as a painter's colour, it will be only briefly mentioned here. Mountain green, or ground earthy malachite, is found in beds and lodes especially in Rhenish Prussia, Nassau, the Harz, Thuringia, Silesia, Tyrol, Hungary, Spain, England, Sweden, Norway, America, &c., in various shades and degrees of purity. The best kinds come from Hungary and Silesia, and are prepared by repeated grinding in wet mills, or, if possible, are ground dry in ordinary mills to a fine, more or less bright blue-green powder of low covering power. It cannot resist atmospheric influences. In Russia it is still sometimes used for painting iron roofs, and very pure kinds are occasionally employed as oil colours in simple cases. Pure native malachite has the formula $Cu_2CO_4 + H_2O$.

V.—BROWN EARTH COLOURS

a. Umber, Chestnut Brown (*Burnt Umber, Velvet Brown*)

True umber is really brown ochre, but gradually the name has been extended by merchants and manufacturers to similarly coloured bodies which approximate physically to lignite, or are identical with that substance, and the term "umber," therefore, is now a very comprehensive one. Originally it was applied to a substance formed by the decomposition of manganiferous iron ores, and very similar to ochre in chemical composition. It is light reddish brown to greenish brown in the crude state or levigated, but bright brown-red to very dark brown when calcined, and with about the same covering power as ochre—properties not possessed by the lignite products except in a very slight degree. In the following pages the various falsely-named kinds of umber must therefore be separately treated under a special heading (see "Cassel Brown").

Umber is found in nearly all countries throughout the world, in Germany in a specially pure state near Saalfeld, Könitz, Camsdorf, &c., and less pure and bright on the Rhine, in the Harz, Bavaria, Elsass, and other places. Specially good qualities are also obtained from Sicily, Cyprus, Asia Minor, the Netherlands, &c.

The formation of umber in the brown hæmatite and spathic iron ore mines of Thuringia, where iron ores rich in manganese are found, is probably due to the decomposition of the haematite ore by water charged with air. The resulting decomposition products, of low specific gravity, have been washed away by the water and deposited in rock fissures. Ferrous and manganous carbonates may be supposed to have been changed, with absorption of water, to ferric hydroxide and manganese hydroxide, the latter at the same time being partly oxidised to manganese dioxide, which causes the dark colour, the depth of which increases with the proportion of the manganese dioxide. The decomposition products are mined, and form more or less dense earthy masses, which, after being dried, are ground direct, or, if they contain a considerable quantity of sand, quartz fragments, &c., are levigated. In the former case edge-runners, as well as balance mills, ball mills, and pulverisers, can be used, care, however, being taken to avoid sifting the product, owing to the difficulty of that operation. If levigation be necessary it is performed in the usual way. The various raw products, however, differ in their behaviour under levigation some settling down quickly, whilst others take a very long time, though of about the same specific gravity.

The calcination of umber is a much simpler operation than with all other colours obtained by a heating process, a relatively low temperature being sufficient to obtain the desired shade, on account of the high manganese content and the usually very low proportion of earthy impurities. Therefore, unless very large quantities are treated, special furnaces are generally quite superfluous, being replaced in many colour works by hearths similar to those used for drying pasty earth colours as described in the general part, except that the heating flues are shorter and the fire-clay plates forming the bed are replaced by strong cast iron plates. These latter are fixed so closely in the walls of the heating flues as to prevent leakage, and furnish a perfectly level surface, upon which the powdered umber is spread in a thin layer, the latter being then heated until the desired change is obtained. No definite rules can be given for this purpose, since one and the same kind of umber not only gives a special shade when burnt, but also a product differing in colour according to the temperature employed. Careful preliminary trials must therefore be made, and the only way to regulate the calcining process is to take small samples from time to time and compare them when cold with the desired shade. Even then it is often necessary to blend several batches of the calcined product together.

In this way considerable quantities of umber can be calcined in a relatively short time; but where the quantities are very large the furnaces used for calcining ochres are the best.

The brightness and intensity of shade of the burnt umber depend not only on the duration and temperature of the calcining process, but also on the form and purity of the crude umber and the method of preliminary treatment. Products rich in manganese oxide generally give when calcined brighter shades in proportion to the fineness to which they have been powdered or the care bestowed on the levigation. This specially bright burnt umber is put on the market as *velvet brown*, *chestnut brown*, *manganese velvet brown*, &c., in the state of very fine powder or in lumps. Sometimes certain brands of burnt umber are very similar in appearance to colcothar, and can be sold as such.

Apart from their tint, all kinds of umber, whether raw or burnt, have the same properties as the various ochres, so that there is no need to describe them again.

Umber is used for various purposes. It is used alone or mixed with other pigments—especially artificial mineral colours or lakes—in the wall-paper industry to produce the ground shade, and the fine brands furnish handsome shades of printing colours with good covering power for lithographic and art work. Here also the umber is applied alone or mixed with other printing colours, especially yellow, green, and red. All brands of umber serve as very durable varnish paints, which dry very quickly and hard. Umber is an essential ingredient of weather-proof paints for outdoor use, and gives a specially rich assortment for painting house fronts.

b. Cassel Brown, Cologne Earth (*Bitumen, Coal Brown*)

These pigments, though similar in appearance to very dark brands of umber, are of much lower specific gravity, and poorer in covering power. Moreover, their behaviour on calcination is very different from that of umber, since they burn away in presence of air to a very small, pale reddish grey ash. They must be considered to be a kind of decomposed, soft earthy lignite, and can be obtained from that substance, or even by grinding and levigating coal. Cassel brown is rarely found native in the form of lumps, but mostly as a fine earthy mass, and the preparation is therefore very simple. The wet mass from the pits is dried and ground in a ball mill, disintegrator, &c., levigation being quite superfluous.

Cassel brown is of but small importance as an oil colour, as the paints dry very slowly and are devoid of covering power. It is, however, largely used for wall and fancy paper making, and also as a water colour. It is partly soluble in caustic alkali, and on this property is based its use for manufacturing wood stains. *Walnut stain*, for instance, is prepared by mixing Cassel brown with water in a cone mill to a stiff paste, which is treated with a solution of soda (6 parts of calcined soda to 100 parts of Cassel brown) for a few days in a suitable mixing machine or a wet mill. The resulting mass is spread about ¾ in. thick on wooden or enamelled iron trays, and dried. The mass when dry chips off as small, shiny, dark brown pieces, in which shape it is sold as dry walnut stain.

c. Mixed Brown Pigments

By mixing the above-mentioned brown earth colours together or with other pigments, especially with artificial mineral colours, various shades can be obtained for ordinary painting purposes, as well as for making wall and fancy papers. The different shades of *fawn*, for instance, are mixtures of raw or burnt umber and strong-coloured dark ochres in various proportions. *Bronze brown* is a mixture of raw umber and chrome yellow, and can be toned with Cassel brown, chrome orange, black pigments, green mineral colours, iron oxide, &c., according to taste.* The various *terra cotta* shades are obtained by mixing burnt umber and red iron oxide colours, chalk, barytes, lithopone, zinc white, &c., in suitable proportions. Some handsome olive greens for wall and fancy papers are mixtures of crude umber with green lake pigments, shaded by means of red or yellow lakes. Raw and burnt umber play a more or less decisive part in the manufacture of olive green oil colours, as already mentioned (see p. 255).

VI.—GREY EARTH COLOURS

Although various minerals found native in considerable quantities could serve as grey painter's colours after suitable preparation, they are very seldom used, because it is easier to mix white natural or artificial mineral colours with blacks in order to obtain cheap grey pigments of a pure grey tint and even the same covering power. The few natural grey mineral colours still used—ground slate grey and zinc grey—are only employed for certain special purposes.

a. Slate Grey, Stone Grey (*Silver Grey, Mineral Grey*)

This pigment is obtained by grinding or levigating special kinds of grey *slate*, found in considerable quantities in veins, beds or single lumps, and stock works, or nodules, mixed with iron pyrites, in many parts of Germany; especially on the Rhine and in the Eifel it forms abundant deposits. According to its hardness and purity, the mineral coming from the pits is either treated in breaking machines direct and afterwards ground to a fine powder in ordinary mills, or, more rarely, is ground in large wet mills and afterwards levigated in the usual manner.

The product obtained by one of these methods forms a fine, soft, yellowish or reddish grey powder, and is used as a wash for walls. If it has covering power enough it can also be used as an oil colour, but in this case only in admixture with white mineral colours. Ground in varnish, it dries very hard, and is therefore used as an oil putty for flattening and stopping uneven surfaces of paint, or when thinned with varnish it makes a very durable ground paint. The application of slate grey for this purpose has the further recommendation that the surfaces covered with it can, after being dried, be smoothed down with water and pumice stone.

In England a kind of grey clay slate is used in manufacturing paraffin wax. This slate contains about 67 per cent. of grey ash, which is used as a grounding paint, and also as a stopping.

In the German colour trade the name slate grey is very often applied to a mixture of white clay with mineral black and lampblack pigments, shaded with ultramarine blue, red earth colours, &c., and is used for the same purposes as the natural product.

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* The well-known, permanent and much liked Vandyke browns, working well with any kind of vehicle, are very similar colours. [TRANSLATOR.]

Some kinds of clay slate containing certain quantities of hydrocarbon, sulphur, nitrogen, &c., lose these elements on calcination, and then form a mass of considerable covering power. Similar products were formerly sold in the form of powder as so-called *filling-up*, but now a great variety of mixtures of white, black, yellow, and red mineral colours are put on the market under the same name and for the same purpose.

b. Zinc Grey

A number of very different products are put on the market, all having the same name, zinc grey. Originally the fine metallic powder obtained in zinc furnaces was collected and used as a grey pigment and called zinc grey, but afterwards grey-coloured zinc oxide adulterated by admixtures of carbon was brought forward under this name, and at present various mixtures of zinc white or lithopone and black mineral colours, lampblacks, &c, are also called zinc grey.

Zinc dust, the true zinc grey, is deposited on certain parts of the muffle in distilling zinc, and is put on the market in this condition. It forms a yellowish to bluish grey, very finely divided powder, with about 98 per cent. of metallic zinc and a high specific gravity. On account of its great covering power it is well adapted for use as a varnish colour. Zinc grey paints dry rather quickly, and very hard, especially on metallic surfaces, and therefore zinc grey is principally used for painting machinery, sheet-iron roofs, and similar objects. The coatings are very durable, and successfully protect iron against rust. The covering power of zinc grey is not equal to that of red lead; its pigmentary power, however, is about the same, red lead being also somewhat heavier. The paints dry with an agreeable light grey tint, which however, darkens, considerably after a time. Zinc grey can be mixed and shaded in any proportion with zinc white, barytes, lithopone, &c.

The grey colours sold as *diamond grey*, *silver grey*, *platinum grey*, &c., are zinc oxides contaminated with carbon or intentional mixtures of zinc white, lithopone, barytes, plumbago, mineral and other black pigments, shaded by the aid of ultramarine blue, yellow or red earth colours, &c. These mixtures are manufactured in the usual way in edge-runners, balance mills, or pulverisers.

VII.—BLACK EARTH COLOURS

a. Mineral Black (*Black Chalk, Oil Black, Slate Black, &c.*)

At present only very small quantities of this product are sold, the so-called mineral black, a clay shale containing up to 30 per cent. and more carbon. When suitably prepared it forms a fine, soft, more or less black powder.

Such products are found in a specially pure state in Spain, less pure in Thuringia, near Osnabrück, near Bayreuth, in Switzerland, the Tyrol, Italy, and many other places. They are of a blue-black to brownish black tint, and are mined from lodes and veins. Black shale is seldom pure enough—that is, sufficiently free from gangue—to be dry ground, and is generally, therefore, first rough ground in stamp mills and afterwards levigated or crushed, according to its degree of hardness. Many raw products can be sent direct from the stamp mills to the levigating tanks; others, however, must be finely ground in large wet mills. The levigated product generally settles down easily, and forms when dried in the air a fine soft mass, which readily falls down as a fine powder.

Mineral black is of good covering power, but requires about 33 per cent. of varnish; the paints therefore dry very slowly on surfaces of all kinds. It is useful as a water colour for wall-paper manufacture, and is used for making the grey mineral colours mentioned under the last heading, giving the product a bluish tint. When calcined with saltpetre it detonates, and the residue when afterwards treated with acids yields a white body consisting of silica and alumina, which therefore acts as a carrier of the pigmentary carbon.

Owing to the fact that much brighter artificial black pigments are obtainable in considerable quantities, mineral black is now of very little importance.

b. Graphite, Plumbago, Blacklead (*Stove Polish*)

Plumbago was at one time considered to be a compound of iron and carbon, but is really only a modification of carbon mixed with ferruginous sand. It is found as a mineral in fairly large quantities, but in various degrees of purity, and occurs chiefly as veins in the primary metamorphic rocks, as round masses in granite, gneiss, mica, primary limestone, &c. The most important deposits of plumbago are at Borrowdale and Keswick, in Cumberland, Southern Siberia, Ceylon, near Passau, Marbach, Montabaur (Westernwald), Yps, Bohemia, Moravia, Sweden, &c. The purest blacklead is found in Ceylon, the ash content being 1·2 to 6 per cent. The least pure kinds come from Sweden and Passau (about 40 to over 60 per cent. of ash).

Plumbago (the *Reissblei* of the Germans), like diamond, is pure crystallised carbon, the crystalline form and physical properties being, however, quite different. It crystallises in tables or small plates of the hexagonal or (according to others) monoclinic system. It forms also foliaceous, scaly, or earthy masses, and is sometimes of a fibrous texture. Plumbago has a grey-black tint, with metallic lustre, is quite opaque, unctuous to the touch, makes a grey mark. Whilst diamond is the hardest mineral known (hardness = 10), plumbago is much softer (hardness = 1·5). The specific gravity is 1·8 to 2·5. For purification it is first crushed, levigated, and afterwards treated with chemicals, the ash content being reduced to 1 to 2 per cent. by fusing it with caustic soda or with sodium carbonate and sulphur, or by treatment with hydrochloric acid, hydrofluoric acid, potassium chlorate, and sulphuric acid, or by other powerful chemical reagents. All these methods, however, are difficult to practise on a large scale, owing to a lack of sufficiently permanent vessels wherein the operation can be performed. It is therefore generally preferred to work the purest possible article that only needs mechanical treatment.

Another modification of carbon, very similar to plumbago, is formed in the smelting of iron with coal in the blast furnace, viz., the so-called *blast-furnace graphite.* The formation of this product is based on the property of molten iron to dissolve carbon. When the iron is allowed to cool slowly this carbon is mostly redeposited as a modified plumbago. When the heavy hydrocarbons contained in lighting gas are strongly heated a special modification of carbon, very similar to plumbago, known as *retort graphite*, is formed. This modification, however, is exceedingly hard and dry, and is not used in colour manufacture.

In practice plumbago is classified into two very different forms, *amorphous* and *foliaceous*, of which the first one only is used to any extent for colour purposes. According to the method of preparation, whether only dry ground or more or less carefully levigated, it comes on the market for painting purposes as a powder of varying fineness and appearance. When *ground* the powder is less fine, and of a more blackish shade, *levigated* plumbago being much finer, and exhibiting a high silvery lustre when spread out with a palette knife, on which account it is sometimes called *silver plumbago.* The most suitable kind for colour purposes comes from Bohemia, which nearly monopolises the Continental market. Plumbago has no importance as an oil or varnish colour, except for a dwindling application to iron goods. Statues of stone or gypsum painted with plumbago are sometimes found, imitating a metallic appearance. In Germany and the north of Central Europe plumbago is almost exclusively used for blackleading iron stoves, for which its fire-proof properties render it most suitable. In Russia, where sheet iron is in almost general use for roofing houses, plumbago is used for roof-painting, and is said to be an excellent preventive of rust.

Mixed with white bodies, plumbago gives a quite neutral grey tint, but is not much used for fine painting. Plumbago is, however, an important material in the *manufacture of lead pencils.* For this purpose it is levigated in admixture with clay, the mixture being ground till quite homogeneous in roller mills, then moulded into small rods, and calcined in this state. The varying hardness and the blackness of the pencils depend on the relative quantities of clay and plumbago used and the temperature of the calcining process. For this purpose, of course, only the finest and purest plumbago can be used, the so-called "amorphous" plumbago. Foliaceous plumbago is made into crucibles that are specially strong, and are used, for instance, for calcining organic black pigments. Plumbago being a good electrical conductor, is also used in electroplating; and forms a lubricant when mixed with oil and fat.

The value of plumbago is estimated by its reducing properties. According to *Schwarz*, a given quantity of plumbago is thoroughly mixed with an excess of lead oxide, the mixture is heated in a closed crucible until the lead oxide fuses, and this temperature is maintained for a certain time. The lead regulus formed by reduction is weighed, every 34·5 parts of metallic lead being taken as equivalent to 1 part of carbon = pure plumbago.

c. Lead Ore, Galena

Lead sulphide, PbS, a mineral from which metallic lead is obtained in metallurgical works, has a deep black colour (especially when free from impurities), but turns brownish in shade when ground. It is of no importance for colour purposes, owing to the high price of the colour obtainable from it, and is replaced by the artificial black pigments, which are much brighter and of a much deeper shade. According to Gentele, it was used at one time as a coarse powder, freed from adhering dust, and scattered on varnished surfaces, to which it imparted a metallic lustre. The same effect, however, is now produced by means of variously coloured coarse glass powder.

C.—BLACK PIGMENTS

General

ALL the natural black pigments have a special modification of carbon—namely, the amorphous form—as the colouring principle. Carbon is known in three allotropic modifications: the regular crystalline, perfectly transparent *diamond;* the irregular, foliaceous, crystalline form of metallic appearance and grey to black colour, *plumbago;* and the amorphous form, *coal* (lignite, pit coal).

For colour-manufacturing purposes, the last two forms alone are of interest, but only to a limited extent so far as the native carbon is concerned. In Germany and Switzerland, Italy and France, it is true, there are deposits of minerals containing amorphous carbon in a form which, after suitable treatment (grinding, levigation), can be used in colour-manufacture. The preparation, however, is so troublesome, and therefore costly, as to be impracticable, now that modern skill is able to produce artificial amorphous carbon in almost unlimited quantities in a more suitable state and at much less cost.

Except plumbago, which is in everyday use as lead pencils, natural carbon is of practically no interest for colouring purposes. The artificial black pigments known as carbon black, lampblack (vegetable black, animal black, &c.), are, however, of great importance.

Lampblack is nearly pure amorphous carbon, obtained by burning carbon compounds free from inorganic, fire-proof constituents, so that the artificial black when calcined leaves only a minute quantity of ash, or none at all. Carbon black (*e.g.*, bone black, or Frankfort black), however, is an intimate mixture of carbon and inorganic substances, and is formed when substances of vegetable or animal origin containing carbon and inorganic compounds are burned in an insufficient supply of air. Under these conditions the carbon is not converted into carbon dioxide, but is deposited as carbon. This process is exemplified, for instance, in the production of wood charcoal. Hence when carbon blacks are calcined in the air until the carbon is completely burned a residue of ash is left.

The fact of a flame being able to produce soot under certain conditions, depending on the nature of the combustion process and on the material used, was observed by the ancients, who also used the product obtained in this way as a black pigment.

Carbon is quite an ideal material as a pigment, being not only almost absolutely fast against the influence of light and air, but also against the chemical influences of acids, alkalies, alcohols, oils, &c., so that it is not dissolved or discoloured thereby, and, moreover, cannot be destroyed below a very high temperature. The amorphous state enables the carbon to be very intimately mixed and ground with vehicles (varnish, oils, aqueous vehicles, &c.) of every kind, and gives rise to a very extensive colouring and covering power. Carbon can be mixed with all vehicles and pigments without causing any alteration in them or being altered itself. It can be treated by any known technical methods, except calcination, whilst at the same time the low cost of carbon pigments, at least of the commoner kinds, is of special importance.

a. Carbon Blacks

The modern method of producing carbon blacks is by the so-called dry distillation. When volatile organic bodies—alcohol, benzene, ether, &c.—are heated to the boiling-point they volatilise without decomposition, and can be collected again in exactly the same state as before by suitable means. This is called the process of distillation, and it is only when the vapours are heated much above the boiling-point that decomposition takes place.

If non-volatile organic bodies are heated in closed retorts they are decomposed, with formation of water and of certain volatile carbon compounds (acetic acid, carbon monoxide, hydrocarbon), of a gaseous, oily, and resinous nature, and deposition of elementary carbon. This latter process is termed dry distillation, by means of which the carbon blacks are produced. Like all manufacturing processes, it requires a suitable management. The apparatus and working temperature will depend on the nature of the material treated. The temperature must not be allowed to rise too high, or a vitreous product, difficult to pulverise, will result, whereas it is essential to obtain a porous, soft mass, which can easily be ground. An excessive temperature also lessens the yield, since after the mechanically retained water has been expelled the oily and tarry decomposition products escape from the material, and when the temperature is raised still higher the decomposition of the carbon derivatives begins, carbon monoxide, carbon dioxide, and hydrocarbons being liberated. This means a loss of valuable material; and it is therefore evident that the same raw material will furnish different products, according to the temperature employed. On the other hand, raw materials of different origin require different temperatures for their decomposition and the formation of suitable products, and the apparatus required also differs.

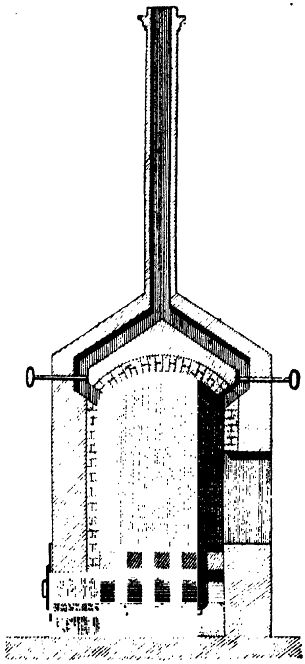
There are two principal methods of manufacturing black pigments:

1. *The heating of organic materials rich in carbon* (wood, bones, &c.) out of contact with air (dry distillation, carbonisation); and
2. *The burning of oily and resinous bodies* containing much carbon in an insufficient supply of air (lampblack).

The products obtained by one or other of these methods differ considerably in appearance and strength, as well as in their other properties, covering power, &c., which difference, of course, influences their various technical uses. In comparison with the products obtained by carbonisation, the lampblacks have a much better covering power. This fact is easily explained by their finer state of division, a consequence of the method of manufacture, the first ones only being mechanically treated. According to the raw materials used, the consequent appearance of the products, and their price, lampblacks are employed as ordinary painter's colours, as also for book illustration and lithographic printing.

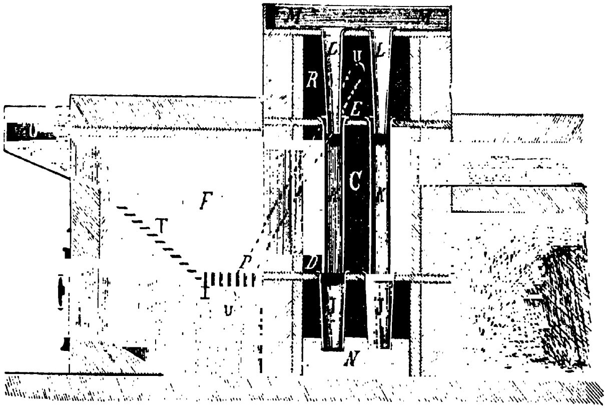
The chief raw material for carbon blacks is lignite, especially the varieties which have a conchoidal fracture, the earthy kinds being useless. Fine bituminous shales are also used. Spent wine must and yeast, vine twigs, fruit stones, spent hops, oil cakes, nut shells, bone shavings, chestnuts, ivory cuttings, various kinds of wood, &c., are worked up to carbon black, the products being sold as *Frankfort black*, *Spanish black*, *bone black*, *ivory black*, *charcoal*, &c. In reality these products do not always correspond with their names. Very little ivory black is really made directly from ivory cuttings; yeast and wine must can be better utilised for cattle food; and it is now realised that the various kinds of lignite can be treated in a manner suitable to their natural properties; hence the trade name indicates the *quality* of the carbon black, not the raw material from which it was made. Wood is built up of cells and vessels, which consist of cellulose, $C_6H_{10}O_5$, and contain the sap of the plant. Freshly cut wood contains 18·6 to 45·2 per cent. of water, whilst wood dried in the open air has only 12 to 20 per cent. of water. European varieties of wood contain, on the average, 50 per cent. carbon, 6 per cent. hydrogen, 43·5 per cent. oxygen, 0·1 per cent. nitrogen, and 0·4 per cent. ash. If wood be heated higher than 150° C. the gases are driven out, water, carbon dioxide, hydrocarbons, carbon monoxide, methyl alcohol, acetic acid, &c., escaping, whilst the charcoal residue becomes richer in carbon as the temperature is raised. According to the kind of wood in question, the output of charcoal (with dry distillation) is 26 to 32 per cent. of the air-dry wood. Deciduous trees give a smaller yield than coniferous wood, bark and branches more than wood from the trunk, while rapid carbonisation results in more gas and less charcoal, the latter being also in a more hygroscopical state.

FIG. 85.



The manufacture of carbon blacks was originally carried on in the same way as charcoal-burning, but the method had manifold disadvantages, and could not furnish a guaranteed pure product. No satisfactory results could be obtained with large brick furnaces, it being impossible to heat the material equally throughout. For this reason the method of producing bone black—viz., heating in crucibles—was resorted to. A simple 7½ to 10 ft. high calcining furnace (Fig.), l 4½ to 7 ft. in diameter, is charged with filled crucibles, which are laid on a fairly large grating. The crucibles are about 16 to 18 ins. high, 1 ins. wide at the bottom and 14 ins. at the top, and are provided with covers, luted at the edges with clay or similar material. 200 to 300 crucibles are placed side by side in vertical rows, but are not packed too tightly. The charging hole is then closed, and the furnace heated slowly, so as to raise the charge to a dark red heat in about twenty hours. The distillation products escape through the leaks in the covers, and are partly burned, thus serving as fuel. The hot gases flow round the crucibles and pass away through the chimney, uniform heating being thereby secured. The dark red heat is maintained for about six hours, and the furnace afterwards allowed to cool down slowly, with exclusion of air, by closing all the openings and fire-doors.

FIG. 86.



All freshly calcined charcoal is liable to ignite spontaneously if exposed to the air immediately after calcination in hermetically closed vessels—*i.e.*, it is pyrophoric. The crucibles must consequently be left a few days until fully cooled, and then be emptied with care.

When carefully worked this method gives perfectly satisfactory results, but is very troublesome and costly, owing to the relatively large consumption of fuel and time. The crucibles, also, have to be frequently replaced. Attempts have therefore been made to introduce a continuous process by the use of retort furnaces of various types, vertical or horizontal retorts, direct firing or heating with superheated steam, &c.

A retort furnace largely used for manufacturing carbon blacks is represented in Fig. 86. The combustion chamber, *F*, is fitted with a step-hearth, *T*, suitable for lignite, with a small plain hearth, *P*, below. *O* is the feed hopper. The flames enter the calcining chamber, *E*, closed above and below by 1¼ to 1½ in. plates, the walls being of firebrick. The top, *E*, bottom, *D*, iron plates are provided with five to six round openings, in which the retorts, *K*, at the top and the cooling cylinders, *J*, at the bottom are suspended by flanges.

The retorts are usually strong cast-iron pipes 5½ ft. long and about 8½ ins. wide, though latterly fire-clay retorts of greater dimensions are also used. Above the calcining chamber is an air-tight chamber, *R*, through which a sheet-iron funnel-shaped pipe, *L*, passes into each retort from a feed hopper, *M*, from which the charge is raked into the funnels and falls into the retorts. The lower extensions of the retorts form the cooling pipes, *J*, about 32 ins. long, fitting exactly on the retorts, and dipping about 6 ins. into water, maintained at constant level in a tank underneath the furnace.

From the calcining chamber the furnace gases escape through several narrow vertical openings, *H*, into a horizontal flue 16 to 20 ft. long, by which means the waste heat from the gases can be utilised for drying the raw material spread on the top of the flue.

The operation proceeds as follows: The raw material is pushed from the hopper, *M*, through the funnels, *L*, into the retorts, *K*, and calcined there, the resulting product falling afterwards through the cooling cylinders, *J*, into the water tank, *N*. The gases expelled from the raw material are prevented from escaping downward by the water seal, and are therefore compelled to escape through the annular gap (about ⅕ in. in diameter) left between the end of the funnel and the inside of the retort into the chamber, *R*, and are led through the pipe *U* below the fire bars, *P*, in traversing which they are consumed. The distillation residue collects on the bottom of the water tank, *N*, and by closing the end of the cooling cylinder prevents the retorts emptying too quickly, the residue being pushed on one side when required, to allow a fresh portion of residue to fall from the retorts.

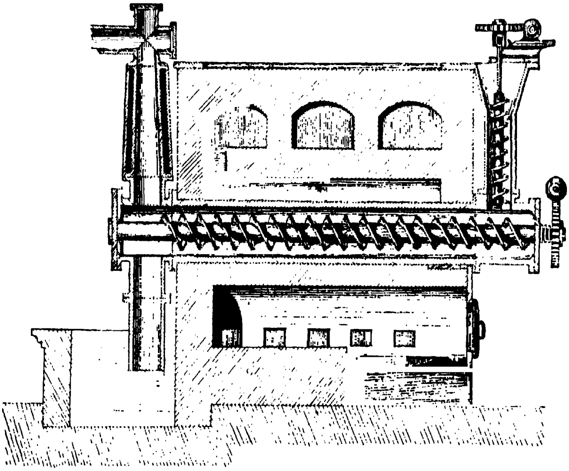
This type of furnace, as used for manufacturing bone black and carbon blacks, varies in construction and number of retorts. In some cases the retorts are similar to those for making coal gas. Retorts arranged in vertical and horizontal rows are also used, and may be fitted with suitable apparatus for recovering the by-products of distillation. Fire-clay retorts are also used.

For work on a large scale, three retorts—two below and the third above—may be combined in one furnace. The retorts are about 10 ft. long, with a diameter of 10 ins. to 14 ins. They are closed at the rear end, and are charged and emptied from the front. From each retort the products of combustion are led through a pipe to a common receiver for collecting the tar and water, the contents of which vessel are kept at a constant level by a flow of water. The gases that are not condensed here are led through a long pipe into a condensing and absorption plant, where the liberated ammonia is fixed by means of sulphuric acid. The gases issuing from this apparatus are collected in gasometers and used for lighting purposes, or are returned to the fire and consumed as fuel.

The heating of a charge takes about six hours. In emptying the retorts the heated, partly burning contents are raked out into a tall sheet-iron cylinder, the cover of which is quickly luted on with clay. The cooling cylinders are placed in the open air, and are not emptied until perfectly cold. The empty retort is recharged at once. Both the charging and emptying must be performed as quickly as possible, to prevent incineration through the influence of atmospheric oxygen. For this reason, too, the finished charcoal is preferably thrown into water, although this method entails a subsequent drying of the product. In calcining carbon blacks the temperature must not be raised above the point necessary for decomposing the organic substances, viz., a dark red heat. For this reason the retorts should be fired with peat or lignite, ordinary coal being too hot.

Halliday constructed a continuous carbonising apparatus for powdered material, so arranged as to keep the product out of contact with the air. A horizontal retort (Fig. 87) is fitted with a worm conveyor, running at adjustable speeds. The raw material is put in at one side of the retort, and is turned over and over and carried to the other end of the retort by the conveyor, so that all particles are brought into contact with the hot walls without being coked by undue contact or overheating. The other end of the retort is fitted with up- and down-cast pipes, the products of combustion passing away through the up-cast pipe, whilst the carbonised residue falls through the down pipe into a water tank, where it is cooled at once. This apparatus evidently has many advantages in comparison with the others mentioned, but it is an essential condition that the raw material should be introduced in a carefully pulverised state. The speed of the conveyor must be regulated according to the nature of the raw material, so that the latter is not heated to a greater extent than is required for carbonisation. Heat is applied to the whole length of the retort—below by direct firing, above by the escaping flue gases.

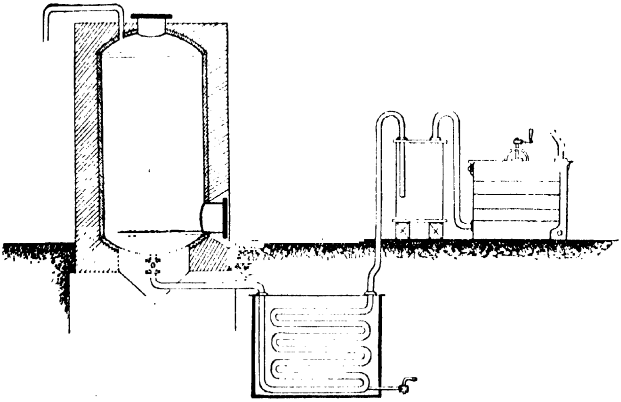
FIG. 87.



To avoid overheating, which is very liable to occur with direct firing, and would convert the soft, porous coal into hard graphitic coke, retorts are constructed for heating with superheated steam or furnace gases. The *Nepp* retort is of the latter type, and consists of an iron cylinder placed in a firebrick retort; both are mounted on a cast-iron frame. The heating gases circulate between the walls of the two retorts. Both can be opened by means of handles on the covers. The heated mass is raked out below, and falls into a hermetically closed sheet-iron box, in which the charcoal is cooled before being put into the storage boxes. The products of combustion in the retort escape through a pipe in the top of the apparatus.

Zwillinger constructed an apparatus for use with superheated steam. The retort (Fig. 88) is made of cast iron, and covered with an isolating jacket. It is filled from above, and emptied below at one side. Superheated steam is blown in from above, and the volatile decomposition products are led through a pipe connected with a cooling coil and a washing and purifying apparatus.

FIG. 88.



The apparatus, heated by furnace gases or steam, can be kept at a definite temperature, and therefore gives a uniform product.

The question as to which kind of apparatus to use must be decided according to the nature of the raw material. In the case of materials yielding valuable by-products—for instance, animal residues and other substances furnishing ammonia, certain kinds of tar, &c.—steam or furnace gases will be preferred; but when the cheap recovery of by-products is impracticable, as is mostly the case in small works, direct firing is used.

The carbon black must afterwards be ground as finely as possible. For this purpose the products collected under water must be thoroughly dried, whilst those brands obtained in the dry state must be cooled to such a degree as to preclude spontaneous ignition.

Coarse grinding is first effected in disintegrators or similar apparatus, the product being then ground to an impalpable powder in wet mills.

Filtering, pressing, and drying processes are performed with the same plants and machinery as already described.

Specially purified carbon blacks are produced by extracting the soluble ash constituents with dilute hydrochloric acid, or collecting the charcoal in water acidified with hydrochloric acid. Generally, however, this treatment is unnecessary, and, on account of the high cost, is rarely practised. Moreover, carbon blacks collected under water always undergo a certain leaching of the soluble ash constituents. The product purified with dilute acid is called *Paris black.*

The result of the manufacture of carbon blacks depends on the raw material and the method used. According to *Illgen, Matthey,* and *Koehler,* dried grape husks and yeast give 20 to 25 per cent. of black, whilst lignite furnishes up to 50 per cent. In large works the recovered by-products—gas, wood vinegar, potash—should about pay the cost of manufacturing the black.

The most important kinds of carbon blacks will now be more fully described.

Frankfort Black (*Vine Black, Drop Black, Rebenschwarz, Noir de Vigne*)

In its purest form this pigment is obtained from spent wine yeast. Grape husks, vine twigs, vine wood, and other similar materials also give products of good appearance and fairly good covering power—the cheaper commercial brands. Various intermediate qualities, at corresponding prices, are obtained from mixtures of Frankfort black from wine yeast and the latter-mentioned brands.

Before carbonising wine yeast, the cloudy residue remaining in the casks after racking off the clear wine is distilled, spirit of wine being obtained as the distillation product, only the thick mass remaining in the retort being dried and carbonised. This is most simply done in iron pans fitted with covers and provided with arrangements for removing gas and vapours. The yeast is first evaporated to dryness, the covers being then placed on the pans, and the residue is progressively heated until no more gas or vapours escape. In large works the dry yeast is placed in iron or clay crucibles, closed by luted covers with a small opening only, and heated in a furnace similar to those used for ultramarine. When combustible gas ceases to issue from the openings of the crucibles, the heating is stopped, and the crucibles are allowed to cool. Instead of crucibles, closed iron cylinders or retorts are sometimes used, being placed in rows in the furnace, so as to be exposed to the heat on all sides. This apparatus also is provided with pipes for the gases formed during the heating process.

When the cold crucibles or retorts are opened a very soft, loose carbon is found, which must be washed and sifted to prepare it for sale. The crude carbon contains small quantities of potash and calcium carbonate, derived from the "tartar" in the wine yeast. The potash is removed by washing, whilst the latter, being insoluble in water, remains in the black pigment. Though it can be removed by treating crude carbon with dilute hydrochloric acid, this is rarely done, the amount being so very small that the quality is unaffected.

Mixed with white pigments, Frankfort black, like wood charcoal, gives pure grey tints with a bluish tinge, but has a considerably higher covering power than charcoal, owing to the finer state of division. The finest brands of Frankfort black also serve for copper-plate printing, but are of no use for ordinary newspaper and poster work. It is specially valued as an artist's colour.

Bone Black, Ivory Black, Paris Black (*Beinschwarz*)

The colours met with in the trade under these names in the pure state are, without exception, calcined and finely ground bones. The calcining process is not a branch of the colour trade, but was formerly confined to the preparation of bone black or animal charcoal for refining sugar. The bone black for this purpose is coarsely granular, but since finer particles are always formed, these latter, reduced to a fine powder, meet with a ready sale as painter's colours. The use of bone black, however, has very considerably decreased in sugar works, and will probably soon be abandoned altogether. Hence it is very possible that colour works will be obliged to manufacture their own bone black, the more so because the demand for it in other branches (glycerine, alkaloids, &c.) is small. For this reason the production of bone black will now be described fully.

Commercial bone black generally contains about 10 per cent. of carbon, 84 per cent. calcium phosphate, and 6 per cent. of calcium carbonate; the latter two may therefore be regarded as the carriers of the colouring principle. The bones must be freed from adhering fat before being calcined, since the fat would cover the carbon (which should be porous) with a more compact coating.

For this purpose the bones are boiled with water in large tanks or steamed in a suitable apparatus. In both cases a great deal of fat is removed, whilst a considerable part of the cartilage dissolves as glue. The bones are then washed and strongly dried.

After this first treatment the bones are of two kinds - dense and porous. The former alone can be used for calcining purposes, whilst the porous bones, which contain glue, are used up in the manufacture of size or applied as manure. The denser bones are separated from the porous ones by crushing with large edge runners, the softer parts being reduced to a fine powder, which is separated from the hard bones in sifting machines. The hard bones are then finely crushed by means of stamps, and are afterwards reduced in edge-runner mills, to a uniformly coarse powder, which is calcined.

The calcining is effected either in retorts, to recover the by-products, especially ammonium carbonate, bone oil (animal oil), or else the products of distillation are burned. The best bone black is said to be obtained by the latter method. In Zwillinger's process the bones are calcined by superheated steam; for our purposes, however, the older calcining method certainly gives better results. Iron crucibles holding about 5¼ gallons are filled with the de-fatted and ground bones, and are heated in a furnace by the flame from a lateral grate. Air is excluded from the crucibles by placing them in pairs one above another, and luting all the joints with clay. For this purpose the mouth of the lower crucible is provided with a recessed flange, into which the upper crucible fits. Shortly after the heating has begun the clay breaks, and the gases or vapours issuing from the joints burn and act as fuel. When no more vapours escape the operation is at an end, and the furnace and contents are allowed to cool in the closed state.

In works manufacturing good bone black for paint the re-ground hard bones are again sifted, and the resulting fine bone powder is calcined by a special operation. The resulting product has a deep black colour and very goodcovering po wer.

Bone black is preferably ground in edge-runners and afterwards in balance mills. The various commercial grades are separately produced by bolting the product through screens of various fineness. On account of the hardness of bone black, these operations are difficult, and considerably increase the price.

Carbon blacks are sold as a fine powder, which in the finest brands is impalpable. Sometimes the black is pressed into square blocks, chiefly for use in making paints, and especially in large quantities for boot polishes (blacking). Carbon blacks are less suitable for water colours, but when ground in varnish they give a very deep black, which, however, has the disagreeable property of drying slowly. They form a dull, rather heavy powder of a more or less deep black tint, sometimes having very considerable covering power. The carbon content varies from 14 to 20 per cent.; there are therefore 80 to 86 per cent. non-pigmentary ash constituents. The finest brands are used for copper and steel-plate printing, but to only a moderate extent.

The lignite coke produced in the Thuringian lignite industry (the so-called *Grude*) gives, when finely ground, a black pigment well adapted for painting purposes.*

According to *Peters'* patent, the fragments from electric arc lamp carbons can be worked up to a very good carbon black. These carbons are made of graphite, retort coal, wood charcoal, petroleum coke, tar coke, and lamp-black, with alkali silicates, pitch, or solutions of sugar, syrup, or glue as a binding medium, and with an addition of boric acid, manganese dioxide, calcium, strontium, or magnesium salts; and a relatively considerable part of the carbon pencils remains unburned in the arc lamps. These remainders were generally worked up again with fresh quantities of material, but in Peters' process they are heated in crucibles between 2000° and 2500° C., and plunged in the hot state into oil, where they remain twelve to thirty-six hours. They are afterwards dried on wire gauze at a suitable temperature, and ground to powder in edge-runners or suitable mills. The treatment with oil softens the mass and facilitates grinding. Linseed oil is the best, this being also the chief material afterwards used in making the paint.

For inferior paints the oil can be left out. The carbon fragments can be heated in crucible blast furnaces between 1200° and 1400° C., and afterwards slowly cooled, whereby they become hard. The resulting material, ground to a very fine powder, can be used for manufacturing mastic, tempering steel, &c.

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* Of late the manufacture of carbon black from charcoal has been patented by a Rhenish firm. The charcoal is first treated with caustic alkalies in suitable mills, and afterwards calcined. [TRANSLATOR.]

b. Lampblacks (*Soot Pigments*)

Carbon black and plumbago differ from lampblacks (soot) inasmuch as they contain more or less ash, while lampblack (soot) is almost entirely free from it. Pure soot of an ordinary brand (apart from accidental dirt) rarely contains more than 0·1 per cent. of ash, any larger proportion indicating contamination. In lampblack, as with carbon black, the carbon is artificially produced by an imperfect burning process; but whereas carbon blacks are made from both organic and inorganic bodies, the former alone are used for lampblack.

Lampblack (soot) is the most important colour used in daily life. The consumption of soap has been said to indicate the place of a country in the scale of civilisation; but lampblack would make a better standard for the purpose, in view of the immense quantities used throughout the civilised world in the form of printer's ink for newspapers, books, &c. Lampblack is also largely employed as a painter's colour, in the manufacture of black oilcloth, india-rubber boots, carbon electrodes, crayons, wall and fancy papers, Japan goods, &c. It is used on a moderate scale for cloth printing and as an insulating material.

Before the manufacture of a pure soot was known ordinary chimney soot was often used as a pigment, after purification. *Gloss soot* was the product deposited nearest the fire, and contained tar-like and resinous combustion products, whilst *light soot* was obtained from the outermost parts of the flues and the chimney itself. These two products, however, are now out of use, at least in the colour trade, on account of their low covering power— a result of impurity.

The immense progress of the chemical industries in the last few decades has greatly facilitated the manufacture of lampblack. The organic by products obtained in great quantities in various branches (coal gas, organic colours, lignite distilling, mineral oil industry) offer valuable raw material in large quantities to the lampblack manufacturer, and have raised the industry to an important position.

Resin and the residues from resin and pitch distilling were the oldest raw materials for lampblack making. The originally very simple method of burning the raw material in a suitable way has been gradually modified into highly complex methods, and elaborated to suit the character of the materials and to effect economy of production.

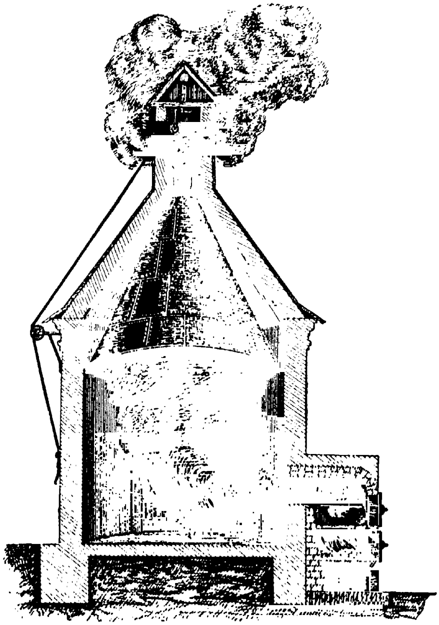
Several varieties of lampblack depend on the differences in the raw materials. *Flame black* is made from solid or viscous material, *true lampblack* from fluids, and *gas black* from gaseous bodies. The first-named is the poorest kind, gas black the best.

Lampblack naturally possesses all the ideal properties of carbon, such as its fastness and workability; it has specially strong colouring power. Being free from inorganic substances, it is exceedingly light and easily worked to a uniform product with all vehicles. In this respect it is superior not only to carbon black, but also every other pigment.

Flame Black (*Flame Soot*)

The most primitive method of making a soot pigment consisted in igniting resin in a pot in a closed room and leaving it to burn until stifled by its own smoke through lack of oxygen. The principle of restricted air supply was therefore adopted, though probably in ignorance. The results obtained by this method were of course very unsatisfactory, the yield being small and the method slow and costly. The product was also of poor quality, the irregular combustion leaving much unconsumed material as empyreumatic bodies, oils, in the black, which was therefore heavy, moist, and malodorous.

FIG. 89.



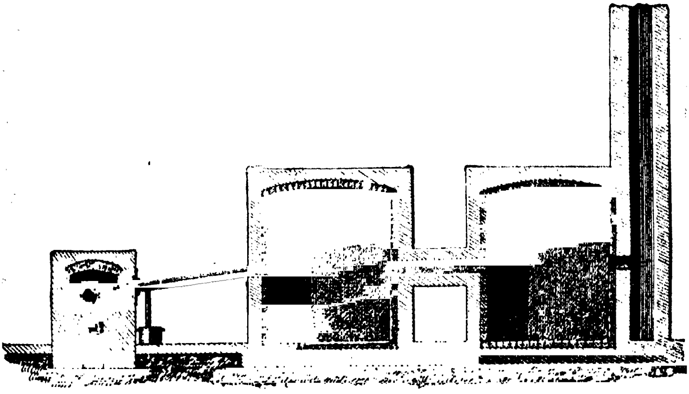
In adopting more rational methods, a plant similar to that for subliming sulphur was used at first (Fig. 89). The generating chamber was separated from the collecting chamber, the latter being a cylindrical tower with a conical roof. The generator consisted of a small building beside the tower, the black passing into the latter through a hole in the wall, whilst the waste gases escaped through a hole in the top of the tower.

The walls of the collecting tower were covered inside with sacking to make them rough and facilitate the adhesion of the black. When the burning was finished the black was removed from the walls by lowering a large hopper from the roof, so as to scrape the black off the sides and cause it to fall to the floor of the collector.

This apparatus enabled the work to proceed continuously and the air supply to be regulated, but had the great disadvantage of causing much waste of black, the collectors getting hot after a time, and the resulting increased draught carrying off a deal of black with the effluent gases.

It was therefore found necessary to provide as much room as possible for the black to deposit, and two or more collecting chambers were placed one behind another, thus forming the rudiments of the existing chamber system.

FIG. 90.



A type of this primitive chamber method is illustrated in Fig. 90. *Thenius's* plant, shown in Fig. 91, is more complicated. The iron grating, *a*, is kept red hot by a special fire (with chimney, *b*) below, whilst oil or melted fat, naphthalene, &c., drops from the vessel *c* through a regulating hole on to the grating, where it is incompletely burnt. The resulting black passes through the chambers, and the waste gases escape by the chimney *d*. The chambers are provided with doors, through which the black is removed.

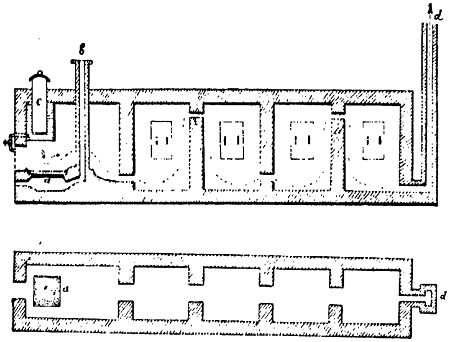
The present great importance of the soot pigment industry has led to a close investigation of the several phases of the manufacture, viz., the *production* and *collection of the black*, and a great many suitable and ingenious forms of apparatus have been devised.

The *apparatus for producing flame black* are various, and adapted for different kinds of raw materials—*e.g.*, tar, tar oil, naphthalene, anthracene, residues from mineral oil distillation, more rarely pitch, resin, &c., *i.e.*, both solid and liquid materials.

While formerly the materials were heated in iron vessels and pans by a separate fire, this system is now abandoned. The small plant formerly used has now been replaced by large furnaces, where the air is regulated in such a manner that it suffices to ignite raw material and keep it burning, no special source of heat being required. The operation is continuous in all cases.

This is not the place to enumerate all the various more or less imperfect plants devised for making soot pigments, it being sufficient to mention the most up-to-date types. The furnaces are horizontal or vertical brick shafts or conical cast-iron furnaces, connected by iron or fire-clay pipes or long brick flues with the collecting chambers. Air is admitted through a certain number of suitably placed openings, the breadth of which can be regulated by dampers, the amount required being sufficient to maintain regular combustion and ensure a maximum separation of carbon from the hydrocarbon material, but not so strong as to oxidise the carbon to carbon monoxide or carbon dioxide.

FIG. 91.



One or more flat cast-iron vessels are charged with the solid or liquid material, a mixture of both being preferable. At one time oil, fish oil, and similar liquids were allowed to drop in thin streams from pipes on to heated iron plates. The oil burned on the plates, but left considerable quantities of coke, and the pipes were also liable to become choked by deposited carbon. Arrangements were also devised for melting solid bodies—*e.g.*, naphthalene—and feeding them through pipes to the firing-place. These frequently proved unsuitable, and the simpler methods of charging have been adopted, the solid, liquid, or mixed material being scooped or ladled at suitable intervals into the heating-pans. These pans are changed after one or two days' work, according to convenience, and freed from the cokey residue. A modern cast-iron lampblack furnace is shown in Fig. 92.

The collector usually serves a number of furnaces, working together or sometimes alternately, when it is considered important not to let the furnaces and flues get too hot. In this case the furnaces are worked in shifts of one or two hours.

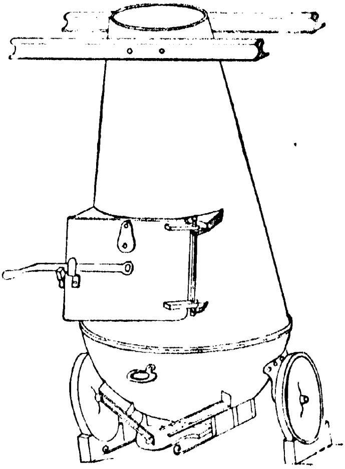
The charging of the furnaces must always be performed very quickly, to prevent any great inrush of air into the interior of the furnace and chambers when the fire-door is opened, owing to the risk of explosive mixtures of air and combustible gases forming and causing great damage to the plant and workmen.

The heat generated in the furnaces is mostly wasted, only a few of the larger works having arranged their plants so as to utilise the considerable heat for steam-raising, drying-rooms, or other purposes.

The *collectors* are also constructed as simply as possible. The plant consists of a series of flues placed one beside or above another, divided into chambers by partitions, and leading to a common chimney. The vapours charged with lampblack describe a tortuous course, the deposition of the black being facilitated by the baffling effect of the partitions.

Fig. 93 shows a ground plan of a modern soot-pigment collecting plant. On the ground floor the combustion products are led from the four furnaces, *a*, through pipes into the hot chamber, *B*, and the first collector, *C*. At the end of *C* the gases are obliged to pass into *D*, and thence they ascend to the upper floor through the opening, *F*, in the roof of *D*—*i.e.*, in the floor of *G*. In *G* the vapours are turned back, in *H* forward, in *J* back again, and are finally led into the chimney, *k*. Partition walls are placed in these flues (as indicated by the lines marked on the plan), by means of which the gases are obliged to describe a zigzag course. On the other hand, doors are provided at *t* in the side walls of the upper floor, which doors are kept closed. *E* is a small lean-to chamber on the ground floor. The dimensions of the flues depend on the quantity of black to be collected in the chambers. As a rule, large lampblack works form rather imposing structures, the more so because the flues are not built very low.

FIG. 92.

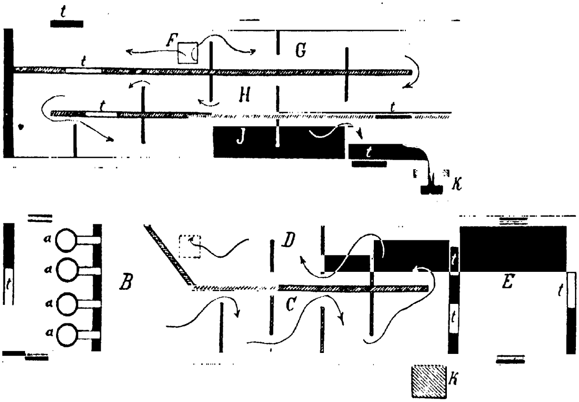


The soot-house is strongly built of brick, and, in order to avoid excessive thickness of the walls, is constructed, at least on the ground floor, of double walls, with an intermediate air space for insulation. This is necessary in order to prevent excessive cooling of the flues, especially in winter, and the consequent loss of draught and the deposition of moist black. There are no windows, but a number of iron valves (closing by their own weight) are provided on the outer walls of the ground floor, to act as safety-valves in the event of an explosion in the interior of the flues. Under careless management an explosive gas may be formed from the air and the distillation products of the raw material.

On each side of the ground floor an isolated iron double door admits to the inside, and two doors lead from the annex, *E*, into the flues. Inside the walls are faced with very smooth, first-class bricks, and the bottom is made of brick or sandstone flags resting on a bed of coke. The hot chamber, *B*, is lined with firebrick. The joints in the walls are scraped out to a depth of ½ in. and pointed with fireproof cement, so as to allow the edges of the bricks to project a little. The building has deep foundations in various places, especially where a high temperature prevails inside, and must be thoroughly dry before being opened for work. No exposed ironwork is allowed in the interior of the chambers, as it is easily corroded by the acid gases, and liable to contaminate the lampblack.

The furnaces are kept at work for two to four days with closed doors, until a suitable quantity of soot has settled down on the inside of the flues. The evening before the flues are to be emptied one door may be opened and left open all night to cool the interior of the chambers enough to enable the workmen to enter for a certain time without danger to health.

FIG. 93.



During the process a uniform temperature must be maintained in the interior of the works, and a constant draught kept up to convey the hot gases from the furnace into the chimney. This draught must not be too strong, but should be kept moderate by the foreman adjusting the dampers for admitting air to the furnaces, as also the openings (usually several) through which the gases pass from the last flue into the chimney. The black settles chiefly in the first two flues, the quantities collected in the others being always less considerable. The black, however, is finer and purer in the latter, that deposited first (especially if the process is well managed) containing more or less unconsumed decomposition products (empyreumatic resins), or distilled oil, sublimed naphthalene, &c. These impurities make the black heavy and moist, and thus cause it to deposit quickly. Even in the end flues the fineness of the black may be impaired if the temperature is not high enough to keep the moisture formed in the process in the state of vapour until it reaches the chimney.

These facts prove the importance of a correct temperature inside the works during the whole process; hence the draught should be restricted during night time to prevent excessive cooling of the flues when the work is to be continued next day. The regulation of the air supply to the furnace and the outflow of gases into the chimney must be adjusted to the requirements of the material, the weather, the state and direction of the wind, and to the topographic situation of the building.

In spite of all care, however, the gases issuing from the chimney will still contain lampblack, and a certain loss always ensues, which is the more serious because of the inconvenience it causes to adjacent property, and is a frequent source of complaint. No perfect remedy has yet been devised. Large filters of sacking have been put across the end flues to retain the black whilst allowing the gases to escape, but these filters soon get choked, even if frequently beaten, and the progress of the work is obstructed. In addition, the heat soon destroys the sacking. Various kinds of wire gauze have also been tried, but these also choke up quickly.

Amongst other screening devices, that by *John* and others similar to it consist of a variety of Venetian blinds placed in the last partition before the gases enter the chimney, and so adjusted that the gases impinge on the sloping metallic strips of the blind. The particles of black collect in flakes of various sizes, and fall down on the other side of the blind, whilst the gases pass through easily. The apparatus works satisfactorily in boiler flues, &c., but not in the case of lampblack free from ash. *Werner von Siemens' spiral deflectors* are said to give better results, the centrifugal motion imparted to the black causing it to settle on the walls of the spiral. The spiral is jacketed by a second pipe, and as the gases pass from the spiral into the jacket the particles of black are driven against the wall of the latter and fall down to the bottom, and the purified gases escape.

According to *Grimm's* patent, the flow of the heating gases is checked by reversing it inside the chimney. The black strikes against the wall at the turning-point, and is driven into a spiral pipe.

In other methods the gases are drawn by exhaust fans through a water seal, which retains the black on the surface. The latter, however, though it will not mix with the water, will absorb moisture during prolonged contact, and becomes damp.

According to the experiments of *Lodge*, high-tension electric currents are said to separate the lampblack from the gases, but this method can scarcely be used in practice, owing to expense.

Although it is certain that in many cases the gases can be freed from the lampblack to a certain extent by mechanical appliances under favourable local conditions, the problem has not been properly solved.

According to the capacity of the furnace and the dimensions of the collecting dampers, the process lasts three to five days, and the lampblack is then taken out. This should be done as quickly as possible, in order to save time and enable work to be restarted with the smallest delay, and also because the men cannot stay long in the hot chambers. The packing of the lampblack is also a very troublesome affair, owing to the bulky and flocculent nature of the product, so that it is desirable to clear the flues as quickly as possible and get the black into a room where it can be packed in comfort. The doors, *t*, *t*, leading to the annex, *E*, and the outside doors on the first floor are opened. The workmen enter the upper flues first, open the doors (closed during the burning process) in the partition walls of the flues, and scrape all the black into the hole, *F*, in the flue, *G*, by the aid of tools resembling snow-shovels Through this hole, which is fitted with a barrier to prevent accidents, the black falls into the flue, *D*. The doors are all closed again, and the men enter the lower flues, where a great quantity of black has settled down already, and can be swept with soft brooms into the annex, *E*. The doors are then closed again, and the process can be resumed immediately while the workmen pack the black in *E*. In many cases the black is removed from the upper flues only at long intervals—for instance, every three or four weeks.

During this operation the men carry lanterns and wear respirators. As a rule, no other safety apparatus is worn, owing to the great heat of the rooms. Before the men enter the flues the latter must be thoroughly ventilated, and when the work is over the men must have an opportunity of washing themselves properly.

The packing of the black requires a certain amount of skill. The black is filled into sacks, and compressed as much as possible by stamping with the feet. When the volume is reduced by this means, the mass is transferred to large sacks or casks, or to small bags, and pressed by machinery.

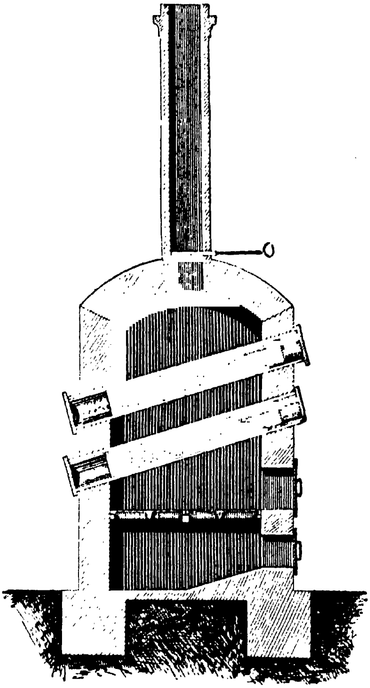
If the building has been properly constructed and in use for some time, so that the black is no longer contaminated with particles from the walls, &c., and if the process has been well managed, the resulting black may be used for all purposes without further purification (as was often necessary in former times) by calcining, sifting, and fanning.

Flame black should be dry and light, and when strongly pressed in the hand must not ball like clay, but fall apart on opening the hand and trickle between the fingers. Heated in a small test-tube, it should give off only a little water, and still less oily distillation products. When a small quantity of pressed black is laid on a filter paper and treated with benzene, the liquor penetrates through the black into the paper and extracts any soluble particles (oil, empyreumatic resin) present, which stain the paper brown or leave a brown ring when the benzene has evaporated. This coloration, however, must be very slight in any case, and entirely absent with good blacks. More precise tests are made by heating a weighed quantity of the black to gentle red heat in a porcelain crucible traversed by a slow current of hydrogen, by means of which contained moisture and empyreumatic bodies are driven out and consumed. The loss in weight gives the quantity of these impurities. To determine the ash, the black is heated in oxygen or is dissolved by boiling with a mixture of strong nitric acid (sp. gr. 1·45) and sulphuric acid (sp. gr. 1·845), expelling the acids by concentration, and weighing the residual ash.

If the black is not well made—*e.g.*, if it contains too much empyreumatic matter and moisture—it must be calcined. Formerly this operation was performed by suffusing the black with petroleum, spirit, or oil of turpentine in an open vessel, and igniting the oil, &c., the impurities being burned off by gently stirring the mass. Another method was to fill a barrel with the black, bury it in soil, introduce a burning rag, and thereby eliminate the empyreumatic matter.

The calcining is now done in pots, as described in the manufacture of carbon blacks, or in tall, narrow iron drums, which are heated in a calcining furnace until no more combustible gas escapes from the cover, which for this purpose has a small opening, or is put on loosely. Calcined black must be quite cold before it can be taken from the calcining pots; and is also pyrophoric. Continuous calcining is effected in the furnace shown in Fig. 94. The inclined calcining pipes, firmly set in brickwork, are strongly heated; the black is introduced at the upper end and moderately pressed with iron crutches, the lower end of the pipes being closed with a cap. When the pipe is filled, the upper end also is closed by a cap containing a hole, and the pipes are raised to a dull red heat. The calcining is finished when combustible gases cease to escape from the hole; and after cooling for a short time the hot black can be transferred quickly into tightly closed iron drums (to prevent access of air), in which the calcination is continued. The process is always a most troublesome one, causing considerable loss, but this loss can usually be avoided by good management. Formerly black produced in defective plant had to be calcined two, three, or even more times. The product was classified into "double calcined," "triple calcined," &c. Black is freed from mechanical impurities by treating it with fans, sifting machines, &c., various types of which are known.

FIG. 94.



Other methods of purification consist in extracting the black with spirit, benzene, or caustic soda, so long as these liquids continue to dissolve colouring matters from the black. In the last-mentioned case the black must afterwards be washed with strong acids, and finally with water. Strong sulphuric acid has also been used for purifying lampblack.

All these complicated, troublesome, and costly methods of purification are now out of date, the product obtained in modern, well-managed works needing no purification, and being fit for immediate use for nearly all purposes.

As already mentioned, the various uses of lampblack require it to possess different physical properties, though the chemical nature is always the same. For certain purposes lampblack of a high specific gravity is preferred; and with this object a number of apparatus are constructed to regulate the combustion, either by a special system of introducing the air, or by partial distillation or combustion of the products of distillation on the heated walls of the apparatus, &c. According to the *Thalwitzer* process, solid, liquid, or melted raw materials are atomised and ignited in a heated arched chamber. When substances are burned in open vessels which easily become hot, so as to give rise to the danger of an oxidation of the carbon (to carbon monoxide or dioxide), the vessels are cooled by being placed in a tank of running water.

A special method has been patented by the *Cologne Russfabriken A.G.* (*Lampblack Co.*). The tar used as the raw material enters a long cylindrical furnace fitted with an internal worm conveyor. The tar is ignited in the feed chamber, placed in the front end, and is conveyed in a burning state to the further end of the rotating cylinder, where it enters a chamber, from which the resulting black is led into the collecting-rooms, whilst the unconsumed residue (pitch, &c.) runs away through a pipe. The proportion of air to the burning tar can be regulated exactly.

Tar will yield 20 to 25 per cent. of black, whilst crude naphthalene gives up to 40 per cent. Resin gives about 20 per cent., pitch 15 per cent. Light oils are not suitable for producing flame black, because they partly distil unburned, and afterwards settle on the black in the collecting-chambers, thus lessening the quantity and value of the output.

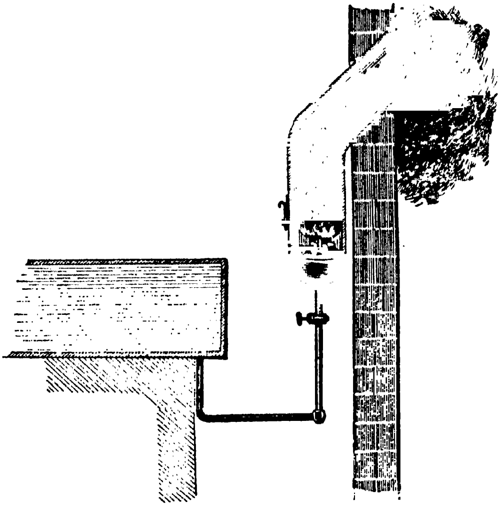
True Lampblack

Lampblack is superior in fineness to flame black, and is also much softer and of a deeper colour. Lampblack is produced from oil in wick lamps similar in shape to the ordinary household petroleum lamp. Large flat burners are used, generally two in each lamp, the wick being adjusted carefully by means of a sliding register, so that the flame temperature, on which the correct production of black depends, can be regulated exactly. Mineral oil is mostly used (solar oil, or distillates from American or Russian petroleum), and the capillarity of the wicks must be adapted to the viscosity of the oil. The lamps are mostly filled from a central tank which communicates with all by means of pipes, a constant level being maintained by a ball-cock. Over each lamp is placed a sheet-iron pipe (Fig. 95), through which only very little air can enter from below—viz., just enough to keep the oil burning. In this pipe the smoke (lampblack) and the products of combustion are led through the wall into a brick chamber (the pipe being bent at an obtuse angle for the purpose), where the bulk of the black settles down. The gases pass from the first chamber into a second and sometimes a third one. Whilst the first chamber is solidly built of brick, on account of the danger of fire, the others are made of sacking stretched on wooden frames, thus allowing the gases to pass through, whilst retaining the black. Finally the gases pass through a series of bags, where the final particles of soot are collected. The sacking walls and sacks are freed from the adhering black by beating them from time to time, so as to prevent stoppage of the draught.

Another method sometimes used consists in retaining the black on artificially cooled metallic surfaces. For this purpose *Prechtl* arranged the lamp flame under hollow sheet-iron cylinders, cooled by a flow of water entering through the hollow shafts. The flame is very close to the cylinders, and the black settles down almost completely thereon, being then scraped off by a suitable knife, so that a fresh surface is continually presented for the deposition of the black. Such as does not settle down is drawn off with the hot gases through an iron cowl into a collecting-chamber.

In another method the flames are situated inside rotating cylinders, cooled by water running over the outer surface. The black settles on the inner walls of the cylinders, and is removed by aid of a suitable knife, which also transports it to the other end of the cylinder, where it is discharged into a collecting-box.

FIG. 95.



According to a recent patent, *Genthe* burns melted naphthalene in wick lamps, the wicks and ducts being cooled to prevent sublimation of the unburned naphthalene.

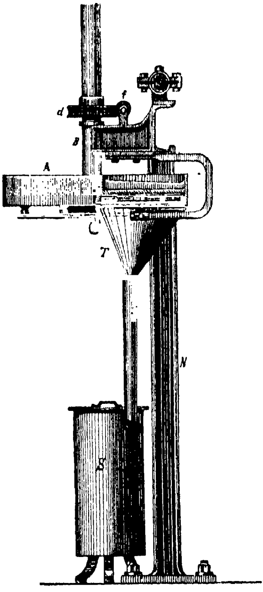
These methods of lampblack manufacture furnish a very good product for certain purposes, but in comparison with gas black, which yields the finest brands of soot pigments, are too costly, and therefore now very seldom employed. The yield amounts to about 16 to 20 per cent. of the oil consumed.

Gas Black (*Gas Soot*)

On account of their high price, the lampblack above described and gas black are only used for certain purposes, especially in making printing inks—lithographic and bookwork printing—Indian inks, and the finest qualities of crayons.

The raw material is burned in the gaseous state, and therefore a supply of gas, either from a gasworks or in a natural state as it issues from the earth, must be available. The bulk of the gas black made is obtained from the latter source, especially in certain parts of the United States, where since 1884 the manufacture of gas black has developed into a very large industry.

FIG. 96.



The gas which issues from the earth is collected, and is used not only as a raw material for making black, but also as a source of power, light, and heat. The employment of such a raw material renders the manufacturing process particularly cheap and suitable. The output of gas wells varies, of course, very considerably, and therefore the gas-black works are constructed so that when the supply fails the plant can be removed at once to the vicinity of a new well and worked there. The output of the American gas-black works is very considerable, one works consuming, according to American statistics, twelve million cubic feet of gas per diem. Since 8000 cubic feet of gas yield 1 lb. of gas black, the daily production of it is therefore 1500 lbs.

The European black industry, of course, has great difficulty in facing such competition, and therefore only a few gas-black makers produce their own gas. In Germany the gas oil produced in Thuringia from lignite—which is also used to produce the gas for lighting railway carriages—is employed for making gas black. The plant for gas-black making is similar to that used in making coal gas. The oil is run in a continual stream into retorts about 6 ft. long and 2 ft. wide. The gas, with the aqueous and tarry products of combustion, first enters a vessel, where most of the tar and water settles down; it is then put through a washer, and passes into a purifying and drying apparatus charged with lime, whence it is led through a meter into the holder, from which it is conveyed through pipes into the burning apparatus. Instead of rich gas containing much carbon, gases low in carbon are carburetted with benzene, &c. in special apparatus, and afterwards burned. Attempts have also been made to burn acetylene to gas black, on account of the deep colour of the product, but without much success.* On the other hand, blast-furnace gas, which at one time was merely treated for the recovery of ammonia, is now also used for making gas black. The plant used for this purpose, viz., for producing and collecting this kind of black, is now very complicated. The *Prechtl's* cylinders formerly used are now chiefly replaced by the *Thalwitz* apparatus, similar to that shown in Fig. 96. The actual collector is the plate *A*, about 32 ins. in diameter, which has a projecting rim top and bottom, the latter to keep the draught from the flame and to retain the black, whilst the upper one holds the cooling water, which is replenished from a pipe as fast as it evaporates. The under side of the plate is smooth ; and five to seven gas flames, supplied from a common pipe, are placed underneath, the black being deposited on the slowly rotating plate. The black is removed from the plate by a scraper, and falls through the funnel, *T*, into the collector, *S*. In the middle of the plate is a hollow vertical shaft, which serves the double purpose of removing the hot gases from the flames and supporting the worm wheel, *F*, which imparts the rotary motion to the plate. The whole is mounted on the iron pillar, *N*, and the casting, *B*, which supports the hollow shaft. The burners are of the Argand type, and enable the admission of air to the gas to be regulated in such a way that the quality of the product can be varied as desired. The larger the amount of air, the smaller the yield of black, but the product is finer and better in colour. The work is continued day and night. About 280 cubic feet of gas are consumed in twenty-four hours, yielding 1½ to 3 lbs. of gas black, according to the quality desired. Each gas retort of above-named dimensions supplies enough gas for about thirty sets of the Thalwitz apparatus. 1 cwt. of gas oil gives about 1000 cubic feet of gas and 5 to 8 lbs. of gas black (according to quality).

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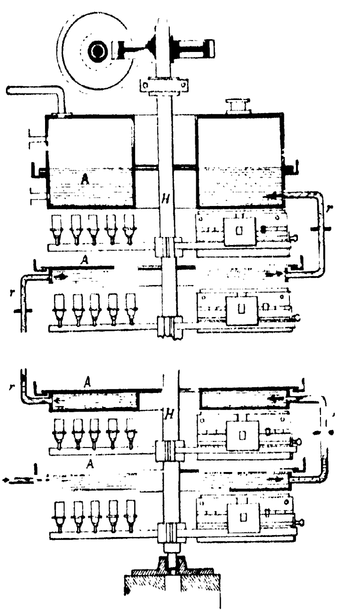
* As a matter of fact, on account of great difficulties, some Continental makers have already abandoned the manufacture of acetylene black, in spite of its high-class properties. [TRANSLATOR.]

Fig. 97.



The plant devised by *Robert Dreyer* also merits special mention, on account of its ingenious construction, especially the model which, in addition to producing a considerable quantity of gas black, also utilises the heat of combustion for raising sufficient steam to work the plant, with a surplus for other purposes (Fig. 97). The shallow water tanks cool the burner flames, and are connected with each other by the pipes *r* and with the upper closed tank, *A*, forming the steam chest. The whole forms a boiler, the several parts of whic ted. The gas flames are rotated under the cooling vessels by the shaft, *H*, which also actuates the scraper and collecting-boxes. The shaft, *H*, is hollow, and supplies the gas to the burners. The apparatus is said to generate about 1 h.p., one-half of which is consumed as motive power. There are 168 flames, which in twenty-four hours burn about 14,000 cubic feet of gas, producing 70 to 90 lbs. of black. The whole plant is enclosed in a strong building, provided with a chimney in the roof for the escape of the waste gases.

Some of the gas-black plants used in America are very primitive, the flames merely impinging against stone plates, from which the deposited black is scraped off at intervals. In other works complicated machines are used, principally of the cylinder type.

The black industry has been thoroughly investigated in the last few years in all its details, and various improved burners have been constructed to increase the output of ordinary flame black, for instance, or to produce black of a specially dense structure or high specific gravity. A series of methods for this purpose have been patented by *Wegelin*.

Frank produces carbon by allowing carbon monoxide, carbon dioxide, or derivatives containing these bodies to act on acetylene or carbides, the mixture being passed through heated pipes or exposed to the electric spark.

Electricity is also used for black-making—for instance, by *Houbon le Raincy*, who decomposes acetylene and hydrogen by electricity, with exclusion of air, and under pressure in a closed vessel, the resulting hydrogen being utilised to displace the air and to dilute the acetylene.

Morani compresses a mixture of air and acetylene (also in presence of an exothermic gas) under a pressure of four atmospheres, and decomposes it by electricity, an explosion pressure of fifteen atmospheres being generated, and carbon deposited.

Berger and Wirth burn a mixture of acetylene and air in specially constructed burners.

The Elektrizitäts A.G., late Schukert & Co., of Nüremberg, has a patented method for producing finely divided black pigment from acetylene or alkaline earth carbides, halogen acids or their derivatives being obtained at the same time. Acetylene is exposed to red heat in presence of a halogen derivative of carbon, or a carbide is similarly heated with a halogen substitution product.

Various attempts have been made to devise appliances for catching the black that does not settle down in the collecting-chambers and escapes through the chimney, but without much success in the case of fine black free from ash, owing to its low specific gravity.

Ogilvy, of Cincinnati, has a patent for causing the flame to impinge against the surface of water, the black settling on the water and being recovered by filtration. The surface of the water may be still or in motion, and the flames fixed or movable. Solutions of hydroxides or salts added to the water are said to facilitate the deposition of the black.*

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* A process giving a gas black of especial high value has just been patented. It is based upon the decomposition of hydrocarbons by explosion. [TRANSLATOR.]

D.—ORGANIC COLOURING MATTERS

AND THEIR UTILISATION IN MAKING LAKE PIGMENTS

THE materials for colour making we have hitherto taken into consideration are exclusively of an inorganic nature, their components being derived from the mineral kingdom, either directly or by the aid of chemical processes. The organic world, too—the animal or vegetable kingdoms—contributes to the colour manufacturing industry. Though up to the middle of the last century the quantity and selection of pigments from organic materials were limited, their technical application has nevertheless been known as long as that of the inorganic colours. Apart from the pictures transmitted to us from the earliest periods of antiquity, fragments of coloured materials made by the Indians, Persians, Syrians, Egyptians, Mexicans, and Peruvians have been found, and can be shown to have been coloured by processes very similar to those in actual use, and with colouring matters belonging to the animal or vegetable kingdom. Even in the books of Moses purple is mentioned as the colour of the priests' vestments, and in the displays given in the Roman circuses the competitors were distinguished by their differently coloured dress. The ancient Britons on the warpath coloured their bodies with woad, a blue vegetable colouring matter.

Legend tells us that the juices and blood of a purple snail bitten by dogs gave the first incentive to the dyeing of cloth. It is historically certain that alkanet, woad, indigo, madder, broom, gall-nuts, and various lichen colouring matters were used technically by the ancients—*i.e.*, that the process of dyeing was well known.

Turning to the organic colouring matters, we shall here use the term "colouring matter" in a strict sense—*i.e.*, a material used for colouring purposes. The organic colouring matters given are, in the proper sense of the term, "colouring principles," not "colours" in the sense used for inorganic pigments. These latter are almost exclusively used in a suitable vehicle or medium, and applied to the surface of the material to be coloured. The compact mass of the colour covers the surface, and the colour and vehicle act together in masking the original shade of the surface—the effect is the result of mechanical action. The material in question is therefore not coloured in the proper sense of the word; it is only covered with an opaque coloured coat.

With the organic colouring matters the conditions are entirely different. In the dry state these substances also are coloured bodies, but this coloration is often quite different from that exhibited when they are dissolved in water or alcohol. Only a few organic colouring matters possess any real covering po[illegible] as a rule their aqueous or alcoholic solutions, or suspensions, have no pigm[illegible]tary effect when applied to other than pure white surfaces. The organic colouring materials are essentially glaze colours, and for most purposes they become efficient when incorporated with other bodies, constituting a ca[illegible] or base of their pigmentary power. Hence their application necessitates a tinctorial process, by which they are fixed on a usually white—colourless—foundation. This base may be a mineral body, in which case the products form the so-called pigment colours, or it may consist of vegetable or animal fibres, in which event we have the processes of cloth dyeing or cloth printing. These two processes form the most important uses of the organic colouring matters.

The fixation of the organic colouring matter on the base is usually effected by chemical means, the colouring matters being suitably precipitated upon the base or developed on it.

Cloth dyeing and printing is a special branch, and of only small importance here, our main concern being with the pigment colours, which are known in the trade as **lakes** (lake colours), and are applied in the same manner as the inorganic colours.

The organic colouring matters are classified into the following principal groups:

I. **Natural colouring matters.**
  1. Of *animal origin.*
  2. Of *vegetable origin.*

II. **Artificial colouring matters.**
  Coal-tar colouring matters.

These latter colouring matters are obtained from coal tar (lignite tar and the petroleum industry also now furnishing the raw materials in certain cases). These artificial colouring matters are therefore also vegetable derivatives, and the coal-tar colouring matters may be regarded as the representatives of the brilliant tints which ages ago beautified the vegetation whose fossil remains we are now able to utilise in the form of coal.

The term "aniline colouring matters," very often applied to coal-tar colouring matters even by colourmen, is wrong. Aniline colouring matters are, of course, always coal-tar colouring principles; but all the coal-tar colouring matters are by no means aniline colours, the latter being merely the first to be obtained from coal tar.

The colouring principles of the vegetable and animal kingdoms m[illegible] exist ready formed in the organisms whence they are extracted; and [illegible] when they are only in a preliminary condition they can be elaborated [illegible] simple means. The method of extraction from the raw material is also very simple, as a rule. The coal-tar colouring matters, however, are never found as such in coal tar, the latter only furnishing the raw material, or so-called medium or intermediate products, from which the colouring matter itself is manufactured by complicated and tedious chemical processes. Hence three different important industries principally contribute to the manufacture of coal-tar colours: the coal-gas industry furnishes the raw material, viz., the coal tar; the highly developed industry of the intermediate products, in which the necessary chemical compounds for making the colours are produced from the coal tar in a suitable state, and partly prepared so as to be in a condition available for the coal-tar colour manufacturing proper.

Whilst, as already mentioned, many of the vegetable and animal colouring principles have been known and applied from the earliest times, the coal-tar colours are the products of modern chemical science, and their manufacture was begun in the middle of the last century. The industry, however, has grown to such an extent during its relatively brief existence that in comparison with its products the inorganic pigments are of only very moderate importance.

In very many cases natural colouring principles have been displaced by artificial ones, usually of greater brilliance, and manufactured on a large scale, according to exact processes, which afford a better guarantee of uniformity in the shade of the products. The raw material of the artificial colouring matters is always available, whereas the supply of the materials of animal and vegetable origin is restricted to certain periods. Hence the artificial colouring matters are usually cheaper, and can be obtained in any desired quantities. In many cases the chemical composition of the natural colouring principles is exactly the same as that of the artificial ones by which they are displaced—*e.g.*, madder (alizarine) and indigo. The chemical composition being identical, the properties, especially fastness to light, air, and chemical influences, must, of course, also be the same, and the artificial product forms a complete substitute for the natural one. In general this chemical identity does not exist, but in most cases the artificial products have the same powers of resistance. Most of the products in both groups do not stand very high in this respect, and unfortunately the most brilliant shades are generally the least resistant. As a rule, however, it is quite erroneous to suppose, as is sometimes done, that the fastness of the artificial organic colours is inferior to that of the natural colours, some of them being even superior in point of fastness to light and air.

With regard to the nomenclature of the organic colouring matters, the same lack of system is found as in the case of the inorganic colours. Whilst a large number of strange names, such as those indicating the animal or vegetable origin of the products, may be more or less admissible, the numerous fancy names devoid of meaning only lead to confusion and uncertainty in the trade. In most cases short scientific or historical names—rarely fancy names—have been adopted in the place of the often very complicated names based on the chemical composition of the products, which are mostly quite incomprehensible to the general public.

The application of the organic colouring matters will be discussed more closely later on, after they have been fully described, so as to facilitate comprehension of their manifold uses and technical applications. At present we must consider a particular form in which the organic colours are put on the market, namely, the *lake colours*. In this form the organic colouring matters are available for all kinds of painting, and the colours, especially the natural colouring principles, are very often prepared in this form from the raw material.

A lake is formed when an organic colouring principle is fixed on a white (colourless) or coloured mineral body so that the product constitutes a uniformly coloured mass of a certain power of resistance. Lake colours must in particular be fast to water—*i.e.*, the lake made from the aqueous solution of a colouring matter must stand washing without parting with its colouring principle to the washing water. A lake, therefore, consists of the colouring matter and its carrier or base. Of this most simple type with two components, however, only a few examples are known, viz., those possessing a certain chemical affinity between the colouring matter and the base, so that the two combine, and the colouring matter is consequently fixed on the carrier. In most cases the fixing of the colouring matter must be effected by a secondary chemical reaction, the aqueous solution of the colouring matter being mixed with the base, and one or more precipitating agents (acids, alkalies, or dissolved salts) afterwards added. In this way an insoluble coloured mass is produced, and at the same time is precipitated on the base. Sometimes the base and the colouring matter are precipitated simultaneously. In certain cases saline solutions are added to the precipitating agents for toning purposes.

In consequence of the very divergent chemical properties of the organic colouring matters, the methods used for fixing and precipitating the colouring matter on the base vary considerably. This will be fully discussed in a special section. As a typical example, a simple scarlet lake may be given, the base consisting of artificial barytes, china clay, common clay in a state of suspension, freshly prepared aluminium hydroxide, or a mixture of two or more of these materials. The solution of scarlet colouring matter is added to this base and well stirred. A solution of barium chloride is used as the precipitating agent, and fixes the colouring principle on the base in the form of an insoluble barium compound. The product, after being washed, dried, and ground, forms a scarlet powder, or scarlet lake.

As already mentioned, the carrier may be one or several suitable bodies, according to circumstances. The most suitable base for lake pigments is aluminium hydroxide, this base giving the purest and most brilliant, perfectly transparent lakes, of great importance in the graphic arts and as artist's colours. The three-colour printing process, now practised in such a high state of perfection, depends upon the use of perfectly transparent lakes. Such products are, of course, generally the most costly lakes. For many purposes, however, this transparency is not only unnecessary, but also unsuitable—for instance, in decorative painting, wall-paper printing, &c.; and in other cases, again, it is found desirable to reduce the cost of the lakes by the addition of cheaper material—*e.g.*, mixtures of alumina with china clay, gypsum, barytes, lead sulphate, green earth, &c. ; or the alumina may be omitted, and then the products have very little transparency; lead sulphate, &c., will give perfectly opaque colours, which are also for the most part cheaper. The cost of a lake is, however, primarily determined by the colouring matter used, and not by the base. Lakes are put on the market in the form of a dry powder, irregular small lumps, and in certain regular shapes—drops, cones, tablets, &c.—and for many purposes, especially wall-paper and fancy paper manufacture, the lakes are supplied in paste form. The plant for manufacturing lake colours is the same as already described in the section on mineral colours.

In the *dyeing industry* the base to be coloured consists of vegetable or animal fabrics—linen, cotton, wool, silk. If these materials were rubbed with a mineral colour—for instance, chrome yellow or iron red—they would be apparently stained, but on washing or simply rubbing the fabric all the mineral colour, being only superficially applied, could be easily and entirely removed.

Properly dyed fabrics can be rubbed, beaten, or washed in water without parting with any of the colour. On examining the two materials side by side under the microscope, the one treated with mineral colour will exhibit the single, isolated particles of colour on the surface, whilst the fabric dyed with organic colouring matter is found to be coloured throughout the whole mass.

To bring an organic colouring matter into a suitable state for dyeing purposes it must be in the finest possible state of division, viz., dissolved in water or alcohol, these being the principal solvents for all organic colouring matters. If small pieces of cotton, wool, and silk are dipped in such a solution, all three will be dyed; but they will not all retain the colouring matter when treated again with water. If, for instance, wool be dyed with an alkaline solution of phenolphthalein, it becomes red, but turns white again on being afterwards treated with water, and therefore gives the colouring matter up again. Dyed with magenta, however, the wool remains red even after being washed with water. If silk be used in place of wool, a real dyeing is again obtained with a solution of magenta; but in the case of cotton it will be observed that this fabric is not at all able to retain the magenta. It is thus evident that the animal and the vegetable fibres differ in their behaviour towards the same colouring matter—a circumstance necessarily due to a different chemical composition of the fibres. On the other hand, it can be observed that different colouring matters do not always act in the same way on one and the same fibre, and this, of course, proves a difference in the chemical composition of the colouring matters as well.

Generally the dyeing process needs assisting by other chemical reactions, and only rarely does the colouring matter act directly on the fibre without any further aid. This assistance is given by the addition of materials able to form insoluble compounds with the colouring matter, and to keep the latter fixed on the base.

The application of the organic colouring matters, therefore, is based on two different methods: either the material to be dyed fixes the colouring matter on itself, in consequence of certain special properties, without any supplementary reactions being needed, or else this fixation requires the assistance of an auxiliary chemical reaction. In the first case the coloration is not a mechanical one, and is not to be compared with the above-mentioned coloration by chrome yellow or iron red, but must be regarded as a chemical process, the substance to be coloured and the colouring matter reacting in such a way that a perfectly characteristic compound, a salt, is formed. The same is the case with the coloration by means of adjuncts, only that the compound will be more complex, three or more components—colouring matter, substance to be coloured, and one or more additional materials—being concerned. In these complicated processes chemical and mechanical phenomena occur jointly.

Colouring matters which fix themselves direct on a suitable base are called *substantive* colours. Magenta, for instance is a substantive colouring matter with regard to animal fibres. *Adjective* colouring matters, however, require some external chemical reaction to effect fixation.

A closer examination of the chemical properties of the colouring matters shows that some act like acids, others like bases. They are therefore classified into *acid* and *basic colouring matters*. It is not difficult to form salts from materials qualified in such a way. When acid colouring matters are united with bases, and basic colours with acids, salts are formed, in the same way as lead chromate, for instance, is made from chromic acid and lead compounds.

The process is less simple with colouring matters of unknown chemical composition, or which are more or less inert in a chemical sense. Of these materials the so-called *developing colouring matters* are such as, being insoluble or very sparingly soluble, must be developed from their components on the material to be coloured, or first reconverted by a reducing process into a semi-prepared state, in which condition they are placed in contact with the material to be coloured, and are then re-formed by an oxidising process. Other colouring matters require a preparation of the fibre or the mineral body to be coloured with metallic compounds, which in this case are called *mordants*. These colouring matters are the so-called *mordant* or *adjective colouring matters*. It is very often possible to obtain quite different shades with one and the same colouring matter, according to the mordant used, which fact is extensively utilised in practice. In the case of the so-called *salt colouring matters*, the colouring matter is deposited from the solution by means of Glauber salt, common salt, or other similar chemical compounds, which in the colouring process do not act by chemical means, but indirectly by their presence only. On the *sulfine colouring matters* the colour is formed only after the colouring principle has been absorbed by the material, and oxidised on addition of soluble sulphides.

The elements forming the organic colouring matters are carbon, hydrogen, oxygen, nitrogen, chlorine, bromine, iodine, sulphur, arsenic, and various metals and alkalies. The colouring matters are not only simple organic compounds, but are, as salts and halogen compounds, combined in a great variety of ways with inorganic and mineral bodies.

In view of the great divergence in their properties, and nature and method of their application, it is quite impossible to classify the organic colouring matters systematically on a scientific basis. Hence our desire in the foregoing remarks has been merely to give a general review of the properties of the organic colouring matters, particulars or details being passed over in order to avoid subsequent repetition. The *coal-tar colouring matters*, however, whose discovery and application is based on a systematic scientific research, have been thoroughly investigated, and can therefore be properly classified, as will be done later on.

The study of the coal-tar colouring matters has also furnished theories of the dyeing process, to which we will refer in discussing the coal-tar colours themselves.

PART I

NATURAL COLOURING MATTERS

I.—COLOURING PRINCIPLES OF ANIMAL ORIGIN

1. Carmine

THE *Coccus cacti*, an insect living preferably on the nopal plant, on which it is also reared in other places, is indigenous to Mexico and Central America. The females of this insect are collected shortly before the laying season, and are killed by steam, hot water, or dry heat, the bodies being dried and sold as a colouring matter in the shape of small oval corpuscles, about $\frac{1}{12}$ in. in length, under the name **cochineal** (*cochenille, coccionella*)—the raw material of **carmine.**

The eggs on the ventral side of the insect are covered with a grey dust, which remains after they have been killed by the aid of dry heat. Cochineal produced in this way is called *silver-grey cochineal* (or *taspeada*). On being dipped into hot water, some of the red colouring matter exudes, and dries on the surface of the cochineal, which is then brownish red or dark coloured, and is called *black cochineal* (*negra* or *renegrida*).

Cochineal was known previous to the discovery of America, and although the *Coccus cacti* was already cultivated, cochineal was believed to be a vegetable product until Runscher in 1729 demonstrated its animal nature.

In the beginning of the nineteenth century, the cultivation of cochineal was extended to the Canary Islands, Algeria, Java, and Spain, so that at present a considerable number of different kinds are sold. *Honduras cochineal* is the most valued kind.

Cochineal is packed in rush or bast bags, the so-called *serones*, holding about 160 to 170 lbs. About 65,000 insects go to 1 lb. of cochineal.

The colouring matter of cochineal is **carmine**, consisting of more or less pure carminic acid. The recipes for manufacturing carmine from cochineal are numerous, the best, however, being kept secret. They are based on the fact that hot aqueous extracts of cochineal gradually deposit a very fine red powder on the addition of small quantities of acids or saline substances. The pure carmine is sold as a powder or pressed into blocks.

At one time the *prepared* or *ammoniacal cochineal* (*cochenille ammoniacale*) was used in dye-works in place of true cochineal. For this purpose powdered cochineal is digested with ammonia (out of contact with air), and the resulting paste left to itself for about one month. The excess of ammonia is evaporated by heat, the residual paste being spread out in thick layers on cloths and allowed to dry. Prepared cochineal is sold in lumps or small tablets.

The combination of the colouring matter from cochineal and the other constituents of a decoction of cochineal with alumina—sometimes also tin—forms the well-known **carmine lake** (Florentine lake, Munich lake, Vienna lake, Venetian lake, ball lake, crimson lake, &c.). The precipitation is effected by adding a solution of alum to the decoction of cochineal, followed by sodium carbonate. The resulting aluminium hydroxide precipitates the colouring matter, and forms, when dried, a carmine-red powder of a violet tinge. If a more scarlet-red shade is desired, a little tin chloride is added to the alum solution. The intensity of the resulting voluminous precipitate can be modified according to the needs of the trade, the tint varying inversely with the amount of alum used.

Before the discovery of the red azo colours (see later, under "coal-tar colours") cochineal was chiefly used for dyeing scarlet shades which could not be obtained in the same brilliancy by other means. Various mordants were employed, alumina mordants giving violet-tinged carmine colours, whilst tin mordants furnished scarlet tones. Cochineal is now of much less importance, and is only used as a water colour [in spite of the much faster alizarine carmine, which has the same shade, and even the same brightness—TRANSLATOR], and as a stain for microscopical preparations. Being non-poisonous, carmine is also used for making face powders, as well as for colouring sweets and products of the culinary art.

2. Lac-Dye

Lac-dye and lac-lac are products very similar to cochineal in origin and application. They are obtained from *gumlac*, an exudation product formed on certain species of *Ficus* by the punctures made by a lac insect very similar to the cochineal insect, namely *Coccus laccæ*, the gravid females of which bore holes in the bark of the trees, and become enclosed in the exuding juice, which hardens into resin. The young grow up in the body of the dead mother insect, and crawl out, leaving in the resin the body of the mother insect and a red colouring matter, which is partly used as food during their growth. The branches of the trees on which the insects reproduce their species in the manner described are covered with a brownish-red crust of resin, and are put on the market in this condition as *stick lac*. On beating the resin from the twigs, it breaks easily into small pieces, and is then called *seed lac*, or *grain* if in larger fragments. After melting and purging it from the colouring matter and dirt, this product forms the well-known *shellac*, which is sold in thin scales. Stick lac contains about 10 per cent., and seed lac 2 to 4 per cent., of colouring matter.

Lac-lac is obtained by treating seed lac with a solution of soda or potash, followed by an addition of alum. This product, containing an alumina-resin soap, is not often obtainable now, being little used in dyeing.

A purer product, *lac-dye*, is obtained by treating the alumina precipitate from lac-lac with dilute sulphuric acid. The colouring matter and the alumina are both dissolved, whilst the resin is precipitated. The alumina lake is reprecipitated from the acid solution by an alkali, washed, and dried.

According to other reports, stick lac is treated in Benares with water—by women trampling it with the feet—until the colouring matter is dissolved. The filtered solution is then precipitated with lime-water, and the lime-lake precipitate is washed, pressed, and dried.

Lac-dye is sold in lumps, small tablets, and powder, dark brown to blackish in shade. Lac-dye is used in wool-dyeing, producing scarlet shades, and, especially on addition of tin salt, gives fine bright shades, faster than cochineal dye, but less brilliant.

The colouring matter of lac-dye was believed to be identical with cochineal. *Schützenberger,* and later *Robert E. Schmidt,* however, assigned the tinctorial power to another body, laccainic acid, which can be obtained, pure to the extent of about 2 per cent. from lac-dye.

Laccainic acid, $C_{16}H_{12}O_8$, crystallises in tablets or crusts, is soluble in alcohol, acetone, acetic acid, dissolves sparingly in water, and is decomposed at 180° C.

3. Alkermes (*Kermes*)

Dyeing with alkermes is one of the oldest methods known, and is said to have been practised in the East in the days of Moses. Pliny calls this colouring matter coccigranum, and states that it was employed in purple dyeing. The Spaniards are said to have paid half of their tribute to the Romans in the form of this highly valued dye-stuff. During the Middle Ages, too, alkermes was of great importance, the famous **Venetian scarlet** being obtained from it.

This colouring matter also is derived from an insect (*Coccus ilicis*), found in Persia, of which several varieties are known. In Morocco, Algeria, and Oran the insect is chiefly found on certain oak trees (stone oak and kermes oak), but also on other plants, which are often entirely covered with this insect. The females with young are globular in shape, and grow as large as peas; they are brown-coloured, dusty, and are fixed on the plants by a flocculent mass. The dried bodies are sold in the granular form, and were at one time believed to be vegetable products; hence the old name *kermes berries* (vegetable vermilion).

Kermes gives yellowish-red shades, and the colouring matter is believed to be similar to that of cochineal, certain authors, indeed, claiming it as identical therewith, but nothing definite is known on the matter.

Cochineal has almost entirely displaced kermes, except in Turkey, where kermes is said to be considerably used for dyeing the national cap, the fez.

4. Indian Yellow, Purree (*Purrea Arabica, Piuri*)

This colouring matter is a product of animal metabolism, and is exclusively prepared at Monghyr, a city of Bengal, from the urine of cows, fed on the leaves of the mango tree. The fresh urine, of a bright yellow colour, is boiled down in earthenware vessels, and deposits a yellow mass, which is strained through calico, made into balls and sold in this shape. One cow produces daily about three-quarters of a gallon of urine, giving about two ounces of purree.

Purree is sold in different brands, marked A (best) to G. The balls are bright yellow on the inside, and of a dirty greenish to brownish colour outside.

The colouring principle is the magnesium and calcium salt of the euxanthic acid, $C_{19}H_{16}O_{11}Mg + 5H_2O$. The better brands, A to D, contain about 65 per cent. of euxanthic acid, the poorest brand, G, only about 34 per cent. The less the quantity of euxanthic acid present, the greater is the content of euxanthon, a decomposition product of the acid. Both substances act as yellow dyes, euxanthic acid, however, being the stronger.

Indian yellow is no longer employed for dyeing, but is used as a water and oil colour by artists, and is one of the so-called permanent colours (normal colours).* It is adulterated with yellow aniline lakes or chrome yellow. It is tested by adding sulphuretted hydrogen to the substance suspended in water, a black coloration being produced if chrome yellow be present. On adding hydrochloric acid a colourless solution should be formed, depositing white flakes of pure euxanthic acid. If yellow aniline lakes be present the solution remains yellow. On supersaturating the solution in hydrochloric acid with ammonia a clear yellow solution should be formed.

5. Sepia

Certain species of marine cephalopods, the so-called *sepia* (or ink fish), have a peculiar gland, which secretes a deep blackish-brown liquor, in order to blacken the water for the purpose of defence against enemies, or to facilitate the capture of food. The sepia are caught on account of the so-called *os sepiæ*, an oval concretion of calcium carbonate and organic substances, utilised in the arts and in pharmacy, and also for their flesh, which is eaten in Italy. The liquor in the ink bag is dried, dissolved by alkalies, filtered, and the colouring matter, having been reprecipitated with hydrochloric acid, is again filtered, washed, dried, and ground with gum mucilage.

Sepia serves as a water colour, and is one of the most permanent brown organic pigments known, being only slightly affected by exposure to light.

The chemical character of sepia is not fully known, but it seems to be an organic acid.

The best sepia is made at Rome. [Certain Chinese harbours, however, are the principal sources of sepia.—TRANSLATOR.] It is sold as *natural* and as *coloured sepia*, the latter being toned to a somewhat reddish shade by the aid of a madder lake. An addition of umber can be detected by calcination, and must be considered as an adulteration. In alcoholic solution sepia is employed as "liquid sepia" by artists.

6. Purple Snail

The colouring matter of the purple snail is of merely historical interest, even though the inhabitants of the sea-coasts of Nicaragua and Costa Rica still use certain snails, *Purpura patula* and *Purpura lapillus*, for dyeing purposes.

The colouring matter is contained in a kind of pustule near the head. The pale yellow liquor does not change colour in the dark or under the influence of air, but rapidly turns purple in the light. Spread on cotton, the colour changes to green, then blue, and finally purple, a smell of garlic being noticeable.

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* See later, under "The Application of the Colours," Oil Painting.

If the colour bag of the purple snail is treated with alcohol or ether a golden yellow solution is obtained, turning purple in the air, and depositing a crystalline powder of the same shade. This powder was named *punicin* by Schunck. 400 snails furnish about 7 mg. of punicin.

The colouring matter is of no technical value.

7. Mummy

A colouring matter bearing this name is said to have been extracted from Egyptian mummies, which varies in opacity according as it is prepared from decayed inorganic materials (bones, &c.) or from an extract obtained by solvents (chloroform, benzene, &c.), the so-called "mummyine." The value of this colouring matter is, at all events, chiefly imaginary, being certainly not superior to umber or asphaltum.

There is no distinct recipe for manufacturing so called "genuine mummy"—*i.e.*, a colouring matter obtained from human bodies.

II.—COLOURING MATTERS OF VEGETABLE ORIGIN

The colouring matters of vegetable origin are of greater importance than the animal colours, both in quantity and technical value, even though they are much less employed than was the case before the discovery of the artificial coal-tar colours. We can therefore deal with most of them briefly and pass to the most important ones, which will be dealt with in alphabetical order, not according to their chemical composition.

Alkanet

The colouring matter is obtained from the root of a plant, the *Alcanna tinctoria* (*Anchusa tinctoria*), belonging to the family of Boragineæ, and found in Spain, Italy, Hungary, Syria, the South of France, and the Peloponnesus. Another drug yielding this colouring matter is the root of the white Lawsonia (*Lawsonia alba*), inhabiting the Orient and East Indies. This latter is called *true alkanet*, the first-named *false alkanet.*

The colouring matter, *alkannin* (*anchusin*), is a dark brown-red, resinous body with a metallic lustre. It is obtained from the root by repeated extraction with water, until this latter is no longer coloured. The dried pieces of the root are then extracted with alcohol and the extract acidified with hydrochloric acid. The alcohol is distilled off, and the residue treated with ether, which dissolves the colouring matter. The last acid particles are taken up with water from the ethereal solution and evaporated to dryness. The residue is repeatedly treated with ether, and finally with water, and boiled down again until a dark red, dry, amorphous mass is left. The formula of the pure product is $C_{15}H_{14}O_4$. It is slightly acid, softens to a plastic mass below 100° C., but the real melting-point cannot be exactly determined. Alkannin forms with alkalies a blue solution, and is reprecipitated on acidification.

Alkannin was used for a short time for dyeing and printing silk and cotton. Violet shades have been obtained with alumina as a mordant, and green shades with iron, but the colours were not permanent, fading quickly on exposure to light or alkalies. Alkannin is now only used for manufacturing cosmetics and toilet articles.

Logwood (*Campeachy Wood, Blauholz*)

One of the most important colouring matters is obtained from the wood of *Hæmatoxylon campechianum*, a tree belonging to the family Cæsalpiniaceæ, occurring in Central America, Mexico, and the Antilles, where it often forms large forests. Soon after the discovery of America the Spaniards discovered this wood and colouring matter, and brought them to Europe.

The different kinds of logwood are classified according to their country of origin, but the quality is usually indicated by the port of shipment. The method of cutting the wood also differs in the various countries. The Spaniards first brought logwood from Campeachy Bay, and called it *Lignum campechianum*, or *Palo campechio.*

The Mexican and Central American woods are generally valued more highly than that from the Antilles. The most important kinds are the following (the ports of shipment being also given):

Mexico: Tabasco, Campeachy, Yucatan.
Haiti: Porte de Paix, Cape Haiti, Fort Liberté, Baineh, Acquin, &c.
San Domingo: Monte Christi, Manganilla, Sabanita, &c.
Cuba.
Honduras.
Jamaica: Port Mosa, Kingston, Alligator Pond, &c.
Guadeloupe: St. Lucia, Grenada.

European ports of destination: Hamburg, Havre, Rotterdam, Antwerp, Riga, St. Petersburg, and Liverpool.

The Mexican wood is imported as stout barked logs, sawn on the one side, rough-hewn on the other. Honduras wood is sawn on both sides. Besides the origin of the wood, the age is also an important factor, young wood being less rich in colouring matter than old. The chemical composition of the colouring matters has not been exactly determined; but the colouring matters of logwood and red wood (see later on) are known to be very similar, which is not surprising, since both plants belong to the same family, the Leguminosæ.

At one time the rasped wood was used direct for dyeing, but not always with good results, and is now replaced by the *extract.*

For the manufacture of the extract, the wood is first reduced to small pieces in various ways—cuts crossways of the grain, shavings, coarse powder, &c. (all, of course, by machinery). The colouring matter is present in the wood as a colourless chemical substance, a so-called glucoside. The glucosides are combinations of sugar with other materials, and are decomposed into their components by the action of acids, alkalies, or ferments. Since the plants contain natural ferments, this decomposition ensues if the wood becomes moist, and the wood is also subjected to fermentation by allowing the comminuted fragments to stand for some time in the air, occasionally assisted by damping.

The extraction is performed by different methods:

1. *The American Method.*—The wood is treated in autoclaves at 1 to 2 atmospheres pressure. This method gives the largest yield, but the extract contains impurities—resin, tannic acid, sugar, &c.—which are not favourable to the dyeing process.

2. *The French method* is a simple process of extraction by boiling under ordinary pressure, and furnishes a good extract and satisfactory yield.

3. *The Diffusion Method.*—This process is very similar to that employed in the sugar industry. It is not often practised, being profitable only when worked on a large scale. The yield is smaller than from the other methods, but the colouring matter is of a purer and more uniform shade.

The extract is allowed to stand for some time in large tanks to allow all the impurities—*pied de campêche*, "foots"—to subside. The clear solution is filtered through cloths and concentrated in autoclaves to various strengths. Up to the density 10° B. the extracts are fluid, but those of density 30° to 45° B. in the hot state become solid when cold.

The colouring principle of logwood is *hæmatoxylin*, $C_{16}H_{14}O_6 + 3H_2O$, which forms yellow, transparent prisms, with a sweetish taste, and requires to be oxidised to convert it into the real colouring matter, *hæmatein*, $C_{16}H_{12}O_6$. When hæmatoxylin is dissolved in ammonia it oxidises rapidly in the air, and furnishes a red solution of the ammonium compound of hæmatein, from which the hæmatein can be precipitated with acetic acid.

The resulting colour varies according to the oxidising agents employed. The shades obtained with alkalies are blue-violet, and the solutions furnish with metallic oxides insoluble dark coloured lakes. When copper salts or chromates are used the colours are almost black.

Hæmatoxylin from logwood was first obtained by *Chevreul* in 1810, and was afterwards studied more particularly by *Erdmann* and *Hesse*. When hæmatoxylin is repeatedly crystallised in presence of a little alkali bisulphite it is obtained pure as colourless, columnar prisms, which part with their three molecules of water of crystallisation at 120° C. It dissolves sparingly in cold water, but is readily soluble in hot water, alcohol, and ether. Hæmatoxylin is specially soluble in a solution of borax, forming a syrupy liquid when heated. When exposed to light, but out of contact with air, the crystals of hæmatoxylin turn red without change of chemical composition. Hæmatoxylin solution completely resists the influence of yeast or other ferments. Out of contact with air, hæmatoxylin forms white salts with basic substances, but when air is admitted the alkalies act as oxidising agents and turn it red.

The chemical constitution of hæmatoxylin is not yet clearly known, in spite of the close investigations made by various workers; nor has the fundamental hydrocarbon yet been isolated in a pure state. The formula $C_{16}H_{14}O_6$, calculated by Erdmann and Hesse, is generally accepted.

The actual colouring matter, hæmatein, is obtained from hæmatoxylin by oxidation with elimination of two atoms of hydrogen, the formula being $C_{16}H_{12}O_6$. (Hæmatein must not be confounded with hæmatin, the colouring matter of the blood.)

Hæmatein forms anhydrous crystals. It is very sparingly soluble in water, alcohol, ether, or acetic acid, but dissolves readily in strong hydrochloric acid, and crystallises from this solution in small dark red needles.

Strong sulphuric acid dissolves it. Caustic soda dissolves hæmatoxylin, forming a bright red to purple-red solution, ammonia giving a brown-violet solution. From these solutions the hæmatein is reprecipitated as a voluminous brown-red mass. The ammoniacal solution gives various coloured precipitates when treated with solutions of metallic salts: copper salts give a brown-violet precipitate, stannous chloride produces a violet precipitate, iron a black one.

Points to be considered in *buying logwood* are the age and size of the tree, and the question whether the wood has been freshly cut or kept in stock for a long time. The exact valuation of the wood can only be arrived at by extraction. The moisture is determined from an average sample, a portion being afterwards boiled and employed to dye wool mordanted with potassium bichromate and tartar emetic. The brighter, deeper, and purer the resulting shade, the greater will be the yield of extract. Another test consists in determining all the extractive principles contained in the wood. The percentage of moisture in the wood must, of course, be taken into consideration in calculating the value. The extracted wood can only be used as fuel, all attempts to utilise it otherwise having been unsuccessful.

Logwood extract is sold under different marks—I, II, O, A, B.

At one time Campeachy wood extract was adulterated with admixtures of syrup, extracts containing tannin (for instance, chestnut extract), or with *pied de campêche* ("foots"). These adulterations are rarely practised now. In any case, the value of the extract—*i.e.*, the content of colouring principle—can never be directly estimated from the degree of concentration, the quantities of the other extractives present varying greatly, according to the origin, age, &c. The exact valuation of the extract must therefore be determined by a practical dyeing test in comparison with standard types.

Logwood is specially used for dyeing and printing black and grey shades on calico and wool. For blues it is never used alone, but only for shading other colouring matters. The black dyeing is performed with the aid of an iron salt and with an addition of some yellow colouring matter to kill the blue tone. The resulting iron lakes are not fast to light, alkali (soap), or acid; but a faster black on cloth is obtained by precipitation as a chromium compound. Latterly aniline black and azo black have largely replaced logwood for wool and calico dyeing, but the iron lakes of logwood are exclusively used for black dyeing on silk, a considerable trade being done for this purpose.

The colouring matter of logwood is not much used to manufacture lakes for paints and printing purposes, more brilliant, purer, and faster substances being available. In the manufacture of wall and fancy papers a special kind of colour, the so-called "vegetable bronzes" (Mordoré lakes, or bronze browns), is largely employed—lakes obtained from logwood (and Brazil wood) by a special method.

A solution of the extract and one of potassium bichromate will give a deep blue-black liquor of such power that it may be used as black ink. The extract has also been used as a disinfectant for dressing wounds.

A mixture of logwood extract with chromium acetate, sold as *indigo substitute*, is used for dyeing wool and calico printing.

Chlorophyll

Chlorophyll is the green colouring matter of the leaves and stalks of plants, in which it occurs in the shape of small, lenticular, flattened globules. Though it is the most generally distributed vegetable colouring matter, its chemical nature is not fully known. It seems to consist of two colouring principles, one blue, the other yellow. In autumn the blue colouring matter decomposes, whereupon the leaves turn yellow. When an alcoholic solution of chlorophyll is shaken up with benzene, a blue colouring matter, cyanophyll is extracted, a yellow colouring matter, xanthophyll remaining dissolved in the alcohol. Chlorophyll is not fully developed in plants unless they are exposed to daylight. Plants which grow in darkness—for instance, in cellars—become yellowish white, from a colouring matter, etiolin, which is converted into chlorophyll when exposed to the light, the plant becoming green again.

To isolate chlorophyll from the plant the following method is adopted, according to *Tschirch:* Grass or green leaves free from tannin are extracted with boiling alcohol. The solution is repeatedly filtered, and boiled down to a mucilaginous mass, which is washed with cold water until the washings run away colourless. The purified mass is extracted with alcohol, and the extract concentrated until crystals are formed. These crystals are re-dissolved in alcohol, and digested with zinc dust on the water bath. A deep green solution with red fluorescence is formed, and keeps well if stored in coloured bottles. A bright green lake can be precipitated from this solution with soda on alumina, but is fugitive in the light.

Chlorophyll can also be obtained by treating the green parts of plants for about twenty-four hours with dilute caustic soda, which dissolves out the chlorophyll. The filtered solution is boiled, refiltered, and the chlorophyll precipitated as a grass-green mass by neutralising the solution with hydrochloric acid.

Being fugitive in the light, chlorophyll is of only small practical value. Its chief use is for colouring confectionery, liqueurs, and toilet articles.

Dragon's Blood

This is a collective name applied to a series of very similar deep brown-red shaded resins from certain tropical trees, especially palms, species of *Calamus,* found in India, Sumatra, and the Moluccas. The resin is excreted as granules on the fruits, or exudes from the bark of the trees when the latter are wounded for this purpose. The finest product occurs as small globules (drops or tears), and comes on the market wrapped in palm leaves. Other kinds are sold as flat cakes, sticks, or in blocks, packed in chests.

The best kind of dragon's blood is a homogeneous, deep red, nearly blackish, opaque, inodorous resin, which has a sweetish taste. It is sparingly soluble in ether or turpentine, readily soluble in alcohol, benzene, chloroform, alkalies, oils, and acetic acid, and contains up to 90 per cent. of a deep red resin.

Dragon's blood was formerly used in pharmacy, but at present serves only for colouring spirit varnishes, toilet articles, &c., a deep red. The colouring material has not been closely investigated.

Fustet

Fustet wood is produced by a tannin-containing tree (*Rhus cotinus*) growing in the South of Europe (Italy, Spain, Turkey, Hungary, Dalmatia), in the Levant and Jamaica, partly wild, partly as an ornamental bush. The colouring matter, *fisetin*, which is only found in the heart of the wood, was intimately studied by *I. Schmid*, though *Chevreul* had already isolated a yellow colouring matter, which he called *fustine*. Besides fustine, he thought he had obtained two other colouring matters, a red and a brown one, but Schmid found this to be incorrect.

For the manufacture of the extract the wood is treated with a very dilute solution of soda, the solution being concentrated to sp. gr. 1·041, and allowed to cool. The originally clear solution becomes cloudy on cooling and prolonged standing, the wood extract settling down in the form known in the trade as *cotinin*.

From this extract the fisetin is obtained by boiling with alcohol and a little acetic acid, the dark brown solution is filtered, and an alcoholic solution of acid acetate is added until a bright red precipitate is formed in a filtered sample. The first formed precipitate is of a dirty brown shade, and contains the impurities of the extract, tannic acid, &c. The filtered solution from this precipitate is then freed from lead by means of sulphuretted hydrogen, concentrated to one-half, then diluted with boiling water, and allowed to stand. The fisetin is precipitated from the hot solution in yellow flakes, and can be filtered off. The product obtained from the cold solution is less pure. The fisetin can be repeatedly dissolved in alcohol and precipitated with water until the mother liquor is no longer brown, but yellow. Finally the product is dried at 100° C.

Fisetin crystallises from dilute alcohol as lemon-yellow needles, and from hot dilute acetic acid in deep yellow prisms, which liberate their six molecules of water of crystallisation at 110° C. It is insoluble in cold water, and only slightly soluble in hot water, ether, benzene, and chloroform, but readily soluble in alcohol and acetone. Fisetin has the formula $C_{15}H_{10}O_6$.

The colouring matter exists in the fustet wood as a glucoside tannic acid, *fustino-tannic acid*, which can be extracted from the powdered wood by boiling with water.

Fustet wood was used in former times for dyeing silk brown. It is now only employed for dyeing wool and leather. The resulting shades are orange to scarlet-red, but not very fast to light, and only moderately fast to soap and alkalies.

Persian Berries, Yellow Berries (*Kreuzbeeren*)

Persian berries are the dried half-ripe berries of various species ot *Rhamnus*, and about the size of peas. This plant grows as a bush, especially in Asiatic Turkey, and was formerly also cultivated in Hungary, Spain, France, and Italy. The berries have a bitter taste, an unpleasant smell, are of greenish or brownish-yellow shade, and are hard and wrinkled on the outside.

The rougher and greener berries give a better extract than the glossy, darker ones.

Persian berries are no longer used direct for cloth dyeing, having been displaced by the extract. It contains the colouring principles as solutions, is, however, not very stable in summer, and ferments easily.

Persian berries of the various species of *Rhamnus* contain several colouring matters: *rhamnetin*, in the state of a glucoside; *xanthorhamnin*; another glucoside, *rhamnazin*; and finally also *quercitrin*.

Xanthorhamnin is prepared by the following process: The dried berries are ground in an apparatus like a coffee-mill, and distilled with 85 per cent. alcohol for about ten hours under a reflux condenser. The extract is filtered and left to stand. After one to two days the brown sediment is filtered off, and small yellow crystals begin to separate from the alcoholic filtrate. These crystals are a glucoside, which, after repeated crystallisation, is obtained pure as very small fine needles of a lemon shade. Xanthorhamnin has the formula $C_{22}H_{24}O_{12}$, is readily soluble in water and alcohol, but insoluble in benzene, chloroform, and ether.

To prepare rhamnetin, $C_{16}H_{12}O_7$, the xanthorhamnin is dissolved in water, and the solution is heated for a certain time with dilute sulphuric acid on the boiling water-bath. The sparingly soluble rhamnetin thereupon separates as a deep lemon-coloured powder; this is recrystallised from its phenol solution.

Rhamnazin, $C_{17}H_{14}O_7$, is obtained by boiling commercial rhamnetin with toluene, the latter remaining undissolved, while the rhamnazin separates in the shape of brown needles.

Persian berries are used for dyeing and printing calico as a pure colour, or for shading purposes. The chromium, tin, and alumina compounds are bright, and resist the influence of soaps or chlorine, but are only moderately fast to light. A well-known artist's colour (*Schüttgelb*) is made from mashed or ground Persian berries by boiling them with water and filtering the decoction through cloth. It is then stirred with a solution of alum, and powdered chalk added, which precipitates a bright lemon-coloured lake. Schütt yellow is, however, usually made of a mixture of decoctions from curcuma, quercitron, and Persian berries. It is sold in small cones, and serves as a painter's colour and for staining paper and leather, but is not very permanent.

Chinese Berries (*waifa, Natal berries*) are the dried flower-buds of *Sophora japonica*, and contain another colouring matter, *quercitron* (*q.v.*). They are especially used in dyeing the silken clothes worn by the mandarins.

Fustic (*Brazil Wood, Yellow Wood*)

Fustic is sold in the form of logs (from which the bark has been removed), sawn smooth on both sides, from the stems of *Morus tinctoria*, growing in the East Indies, Central and South America, and the Antilles, where it attains a height of about 150 ft. The wood is hard, firm, and of a light yellow to orange colour. The poorest kind, Brazil yellow wood, is mostly very worm-eaten. The various kinds are classified according to the country of origin and the port of shipment, the principal varieties being Nicaragua, Costa Rica, Salvador, Colombia, Panama, Venezuela, and Jamaica.

Yellow wood contains two colouring matters—*morin*, $C_{15}H_{10}O_7$, very sparingly soluble in water, and the readily soluble *maclurin*, $C_{13}H_{10}O_6$. Morin is present in the free state, but in some kinds (Cuba wood) is combined with lime. The extract is obtained by boiling the rasped or chopped wood in a solution of soda until the solution has the sp. gr. 1·041. The bulk of the maclurin and morin crystallise out from this extract. Maclurin is often found in the wood as a reddish-yellow, crystalline sediment. The extracts made in France and Germany are viscous or solid, but less vitreous than logwood extract. The American extract is hard, olive-coloured, and lustrous, and has a conchoidal fracture.

Morin is best made from the extract by treating this latter for a certain time with water containing hydrochloric acid. The bright yellow solution is filtered from the sediment, and the residue is treated with water containing hydrochloric acid until the liquid is only very slightly coloured. When pressed and dried it forms a brownish-yellow powder, corresponding to about 10 to 20 per cent. of the extract used. It contains a considerable quantity of an amorphous substance as an impurity. This crude product is dissolved in hot alcohol, filtered, and then treated with hot water. The morin separates out as crystals on cooling. The solution is heated again, and then reprecipitated with boiling water as long as any crystalline sediment is formed. The collected crystals of morin are finally recrystallised from alcohol.

Pure *morin* forms colourless, lustrous needles, with a bitter taste. It is sparingly soluble in water, more soluble in alcohol and acetic acid, and insoluble in ether and carbon disulphide. Morin dissolves in alkalies to a yellow solution, from which it is reprecipitated by acids.

Maclurin also forms colourless crystals, has a sweetish astringent taste, and is readily soluble in water, alkalies, and alcohol. It decomposes carbonates, and is precipitated by tannic acid. For this reason it was formerly called *morintannic acid*, until its properties, which are quite different from those of morin, became known.

For dyeing, the extract is very often replaced by a lake made from Cuba wood, the so-called *Cuba lake*, on account of its greater purity. It is an olive-coloured paste, and is obtained by precipitating a decoction of the wood with alum.

Yellow wood is chiefly used for dyeing wool, especially as a ground for logwood-black dyeing, and for printing cottons and woollens. Various yellow shades are obtained, according as a single or duplicate dyeing (one-bath or two-bath method) with alumina is employed. With copper sulphate an olive shade is obtained, with ferrous sulphate a dark olive. The brightest and most permanent shades are obtained by the aid of tin.

Yellow wood colours are generally not very fast to light, and are of a dull to brownish shade. They are fast to the influence of soap and weak alkalies.

In silk dyeing the colouring matter of yellow wood is used for shading mixed colours.

At present the coal-tar colours galloflavin and alizarin yellow have largely displaced yellow wood.

For painting purposes the aforesaid Cuba lake, also called morin lake, is sometimes used. The colour is brighter in proportion as the solution of alum employed is purer and, especially, free from iron. With basic lead acetate too (a solution of sugar of lead in which litharge is dissolved by boiling) a bright yellow lead lake is obtained from the filtered aqueous decoction; but this colour is not at all permanent, and therefore is of no practical use.

Gamboge (*Gumigutt, Gutti*)

This substance is the resin of *Garcinia morella*, a plant found chiefly in the East Indies and Ceylon. On incising the bark a milky liquor which gradually sets hard is obtained. It is collected and stored in bamboo canes. On removing the cane the hard resin is obtained as cylindrical sticks of about 1¼ to 2½ ins. diameter. The dense, homogeneous, brittle resin (conchoidal fracture) is opaque, reddish yellow in colour, and furnishes a bright yellow powder. It is inodorous and has an acrid taste. It softens at 100° C. without melting, gives a yellowish emulsion with water, and is only partly soluble in ether and alcohol.

Poorer qualities of gamboge are of a brownish colour and granular fracture. They are also obtained by boiling the leaves and unripe fruit of the plant.

Gamboge is used for manufacturing a yellow water colour, and sometimes for colouring spirit and other varnishes. It is poisonous, but is used in pharmacy.

Indigo

Indigo is one of the oldest and most extensively used blue colours. Even in the earliest times it was used as a dye-stuff in the Orient, and its importance for this purpose is still based upon its great permanency, which is not surpassed by any other colour, although the recent discovery of artificial, synthetical indigo has nearly displaced the old natural product.

Indigo occurs in Nature in considerable quantities and in various species of plants, more especially the *Papilionaceæ*, comprising various species of *Indigofera* (*I. tinctoria*), chiefly inhabiting India, China, Japan, the Philippines, Central America, Brazil, Java, &c. In Europe, too, the *Isatis tinctoria* (pastel, woad) and the *Polygonum tinctorium* (dyer's knotgrass), plants containing indigo, were formerly cultivated (Great Britain, France, Germany, &c.), but their cultivation has long been abandoned, the yield of colouring matter being too small compared with the true indigo plant. The principal seat of indigo culture is India (especially Bengal), where an indigo-yielding species of oleander, *Nerium tinctorium*, is also known.

Indigo blue is not present in the plant as such, but as a glucoside, *indican*, which probably occurs in all plants yielding indigo. The manufacturing process in indigo factories is as follows: The crop is gathered three times a year, at flowering time—January, June, and September—the leaves being tied in large bundles. Generally the leaves alone are used, containing about 0·5 per cent. of colouring matter. This latter is also present throughout the whole plant, but only to the extent of 0·2 per cent., and therefore the whole plant does not pay for treatment.

The bundles of leaves are sprinkled with water and a little milk of lime or ammonia in large tanks or pits lined with cement, and are left to ferment for a certain time, a copious liberation of carbonic acid and a frothing of the mass being observed. The fermentation process must not continue too long, or the quality of the product would suffer, whilst incomplete fermentation leaves the indican imperfectly dissolved. The end of the process is indicated by the smell, taste, and colour of the liquor, and the formation of a blue sludge, and other signs. When fermentation is complete (in about twelve to fifteen hours, at 30° C.) the colouring matter is in the state of an aqueous solution, the so-called *indigo white*, whereupon the olive-coloured liquor is transferred to other vessels. In these the colouring matter is oxidised by atmospheric oxygen, introduced by beating the liquor with rods, the use of stirring apparatus, an air-blast, &c. When the colour particles coalesce and separate from the liquor this operation also is complete.

During the fermentation in the first tanks the *indican* is decomposed, according to *Schunck*, into *indigotin* and *indigoglucin*, the blue, however, being reduced at the same time to soluble indigo white. This latter is then oxidised to indigo in the second vats.

The indigo settles to the bottom as a fine, somewhat sandy, blue powder, which is washed and boiled once with water. This boiling process serves various purposes. Thus, it eliminates a brown extractive principle contained in the crude indigo; it stops the fermentation and prevents putrefaction, by destroying the micro-organism, the *Bacillus indigogenus*, credited with being the fermentation agent, and, as said, it brightens up the colour. The colouring matter is pressed, dried very slowly and carefully in the air, in order to obtain a light, fine, and superior product.

100 parts of the dried plant yield about 1½ to 2 parts of indigo, containing 20 to 90 per cent. (mean about 50 per cent.) of pure indigo colouring matter, *indigotin*.

Besides the blue, commercial indigo contains indigo red (indigorubin) and indigo brown, indigo gum, mineral substances, and a moderate amount of water.

The best brands are obtained from Bengal and Guatemala. Poorer qualities come from Coromandel, Manila, Madras, Caracas, Brazil, Cuba, Jamaica, Domingo, and Mexico.

A good brand must be specifically light, of a pure blue colour (with only a very slight violet tinge), and exhibit a bright yellowish, coppery lustre when rubbed. The fracture must be uniformly dull, of a pure blue, and show a bright metallic lustre (indigo cuivré, gefeuerter Indigo) when rubbed with a hard body. Pure indigo floats on water, and can be easily and completely dispersed in it without giving a heavy sediment—the formation of which would indicate adulteration. Pure indigo burns easily, and is very brittle.

Indigo blue dissolves with fuming sulphuric acid to a purple-red solution (sulphindigotic acid). Strong caustic potash dissolves it to an orange-yellow solution. It is partly soluble in chloroform, aniline, benzene, strong acetic acid, nitrobenzene, toluene, phenol, acetone, amyl alcohol, stearin, paraffin, and in the heavier fractions of petroleum. On being heated indigo gives off a red vapour. It dissolves in nitric acid to form the yellow colour *isatin*.

It is rather difficult to determine the commercial value of indigo. The moisture content is ascertained by drying at 100°, and should not exceed 3·7 per cent. If the ash content be more than 10 per cent. the indigo must be regarded as adulterated (sand, chalk, graphite, &c.). Starch, gum, dextrin are sometimes found as organic adulterations. If powdered indigo is ground with a little water it must not form a mucilaginous mass, this indicating the presence of gum and dextrin. If the solution in nitric acid turns blue on the addition of potassium iodide, starch is present. Logwood lakes and Prussian blue are also sometimes added to indigo, and occasionally the lumps of the poorer brands are coated with a layer of better quality.

The tinctorial power of indigo is tested by making a trial dyeing with the sample, *von Cochenhausen* recommending the following method: First of all a standard scale is made by converting 1 grm. of really pure indigo blue into sulphindigotic acid with 20 to 25 c.c. of strong sulphuric acid, this solution being diluted with water to 1 litre, of which 1, 2, 3, 4, 5, 6, &c., up to 20 to 25 c.c. are used to dye separate portions (5 grms.) of wool (freed from grease with ammonium carbonate) for three-quarters of an hour, the temperature being raised to boiling point. The samples are dried in the open air after having been cooled and washed, and are kept in boxes out of contact with light and air, in which condition they will remain for a long time unchanged. 1 grm. of the sample under examination is treated in the same way, 10 or 20 c.c. of the solution being used for the trial dyeing, and the resulting colour is compared with the standard types.

The content [illegible] *indigotin* is determined, according to *Ulzer*, by boiling 1 grm. of powdered indigo for ten minutes with 50 c.c. of a 5 per cent. solution of caustic soda and 10 c c. of a solution of hydrogen peroxide. When cold the liquid is diluted with an equal volume of water, and filtered through a dried, tared filter. The filter is washed first with warm water, next with dilute hydrochloric acid (1 : 10), then with water again, and finally with boiling alcohol, until the filtrate is no longer brown, but pale blue; it is then dried at 100° C. and weighed. After being weighed the residue on the filter is incinerated with the filter, and the weight, subtracted from the total weight of the ash, gives the weight of the indigotin by difference.

By the extraction method the indigotin in a weighed sample of commercial indigo can be brought into solution in a suitable solvent, the crystallised indigotin being weighed direct (*Hönig's, Schneider's, Brandt's* methods).

The tinctorial power of indigo can also be ascertained by the reducing method of *Rawson*, which, however, is too complicated in detail to be described here.

Colorimetric methods can also be applied to the examination of indigo.

Of the various kinds of indigo, only those from Bengal, Java, and Guatemala come under consideration for the European dyeing industry. These three kinds, however, are divided into a large number of brands, the good properties of which depend on the kind of soil in which the plants are grown. The experienced indigo merchant can detect the place of origin by distinct characteristic signs and qualities; and there is also a special, though not very perfect, system of classifying the various brands according to the districts whence they come, this being also partly supplemented by marks. For instance, Bengal indigo comprises more than 300 distinct brands, whilst Java indigo has only a few brands, and Guatemala indigo only two. The finest indigo is that made by the Dutch (Java indigo), which has the lowest specific gravity and percentage of ash and extractives. Each of the regularly shaped lumps is stamped "Java."

Bengal indigo, the most important in point of quantitative production, is manufactured and sold by the British. It comes into the market in the form of prismatic lumps, bearing the reticulated imprint of the calico on which they have been dried, and mostly stamped with a distinctive mark. Guatemala indigo, called *sobre saliente*, is one of the poorer kinds. The *Velores* brand (from the same country) is often equal to that from Bengal. It is met with in irregular lumps, and exhibits a characteristic fine green skin, whence its name, "green indigo."

Indigo merchants usually judge the place of origin and the commercial value of a sample by external signs, but this requires wide experience and long practice, and is even then a difficult and unreliable method, so that chemical examination is indispensable.

Indigo is used for dyeing calico and wool, and furnishes the most permanent blue dyes. The method is known as vat-dyeing, and will be described later on.

Indigo was first brought from India to Italy and the Netherlands in the sixteenth century, but the farmers cultivating the woad plant strongly opposed its use. The importation of indigo was prohibited by law in England, and also in Germany (1577, and also in 1654). In the city of Nüremberg the dyers were forbidden to use indigo for dyeing under penalty of death, and it was not until 1737 that the use of indigo was generally permitted.

Pliny and *Dioscorides* were acquainted with indigo, and called it *indicum*. They state that it ranked next to purple, and was used in painting and pharmacy.

The old Egyptians were also acquainted with indigo, and mummies have been found covered with blue wrappings dyed with indigo.

Caius Plinius Secundus (the younger *Pliny*) in his "Natural History" (thirty-five volumes) gives a very exact description of indigo, its manufacture, adulteration, uses, and tests. He mentions, for instance, that indigo heated over a fire burns with a purple flame and gives off a smell of tea. In addition to dyeing and painting, it was applied in medicine for drying wounds, and against cold and fever. A pound sold for 20 denarii. At one time indigo was believed to be a metal. An ordinance dated 1704 gave express permission to miners to prospect for indigo (Indian stone).

An interesting fact, though of no technical importance, is the existence of indigo in the animal and human organism. Indigo has been detected in perspiration, pus, and urine, serving in the latter case as a diagnostic indication of tuberculosis or intestinal trouble.

Indigo is used as a water colour, as also for cloth dyeing, but is not very fast to light.* It is much less suitable for oil colours, as it assumes a dull and blackish-blue tone. In wool and silk dyeing and as a liquid colour use is made of *indigo carmine*, obtained by saturating a dilute solution of sulphindigotic acid with soda. It forms a blue paste with a coppery lustre.

In recent times the importance of natural indigo has declined owing to the successful manufacture of artificial indigo, to which reference will be made later on.

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* Artificial indigo can also be used for lake making. Indigo lakes are absolutely fast and can be produced in various shades with the characteristic lustre. They are especially adapted for producing combined lakes, which generally are very bright and of a specially warm hue. [TRANSLATOR.]

Before artificial indigo was manufactured the yearly production was about 4500 tons, of which quantity India alone was supplying 3500 tons. The total output in 1902–3 was 3330 tons.

The value of the indigo exported from Germany was about £150,000 in 1897, but, in consequence of the manufactured synthetical indigo, had increased to a million sterling by 1903.*

Cutch (*Japan Earth, Katechu, Cachou*)

In Bombay a hard, dark brown, astringent extract, the *true catechu* or cutch, is obtained by boiling the wood of a 16 ft. to 25-ft. tree, the *Acacia catechu*. Another kind of cutch is obtained in Bengal by boiling the fruit (betel nut) of the areca palm. Mention should also be made of the *gambir* or *cubical cutch*, obtained by boiling the leaves and twigs of the *Nauclea gambir* and *Uncaria acida* in water.

True cutch comes on the market in large lumps, weighing from 70 to 90 lbs., which have a greasy fracture. Gambir cutch is also sold as small lumps, 1¼-in. to 1½-in. cubes, which are light yellow inside, dry, and readily friable.

The colouring principle of cutch is *catechin*. It is obtained by treating cutch with cold water and allowing it to stand for a few days, the solution being filtered, and the residue washed with cold water until the washings are nearly colourless. The *catechu-tannic acid*, used for tanning purposes, is obtained in the solution, and *crude catechin* remains, this being recrystallised from hot water, in which it is soluble. Pure catechin consists of fine, white, silky, hygroscopical needles, melting at 217° C. The exact chemical composition of catechu is not yet known, and a number of entirely different opinions have been expressed by various workers.

Cutch is used in cotton dyeing and printing, to produce brown, black, grey, and olive shades, and gives very permanent dyes, fast to light, acids, soap, and even bleaching powder.† Certain brands of catechu are also used for dyeing silk and making wood stains.

Madder (*Krapp, Garance*)

Madder dyeing was practised from the earliest times, and retained its great importance up to the second half of the nineteenth century. Madder is used for producing the famous *Turkey red*. Whereas in and about 1860 approximately 70,000 tons of madder, worth about two and a quarter to two and three-quarter million pounds, were produced every year, the discovery of artificial *alizarine* in 1869 ruined the madder-growing industry, which is now almost entirely abandoned, a small quantity being still cultivated in France for special purposes in dyeing wool [and high-class artist's colours.—TRANSLATOR].

Madder is the dried and ground root of *Rubia tinctorium* and other species of the *Rubiaceæ*, containing several different colouring matters. The principal one is *ruberythric acid*, which is a glucoside of alizarine, and was isolated by *Rochleder* in 1851, by extracting madder with hot water. When ruberythric acid is treated with acids it decomposes into *alizarin* and a kind of sugar. Alizarine was first obtained pure by *Robiquet* and *Colin* from the madder root. Madder also contains purpurin, pseudopurpurin, xanthopurpurin, xanthin, and some other colouring materials.

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* 1907: £1,650,000. [TRANSLATOR.]

† For many purposes cutch is now advantageously replaced by artificial coal-tar colours of recent date; for instance, by the so-called immedial colours (Cassella), the most suitable of which is immedial cutch. [TRANSLATOR.]

To obtain the colouring principle from the madder root, the latter was treated with steam, acids, and other solvents. Various madder products were manufactured in this way, of which *madder flowers* were the most important. These, when boiled with strong acids, furnished *garancin*, which yielded *pincoffin* when treated with superheated steam.

Other madder products are *garanceux*, *madder carmine*, &c. *Alizarine* is obtained from the madder root by a method devised by *Runge*, preferably by extraction with a solution of alum. On treating madder flowers with strong sulphuric acid *madder charcoal* is obtained, from which the extracts (colorine) are prepared.

The madder root pulled from the soil at the beginning of summer is called *summer root*, that gathered during autumn being known as *autumn root*. The roots, which are mostly pulled in the third year after sowing, measure about 8 ins. to 10 ins. in length and up to 4½ ins. thick; they are red-brown and wrinkled on the outside, and yellow red inside. Ground madder is a coarse saffron-yellow powder with a characteristic taste and smell. Storage for some years improves the yield, but it must be protected from light, air, and damp.

In Syria, Asia Minor, Greece, &c., madder is called *lizari* or *alizari*; hence the name alizarine.

Madder was known in the earliest times. *Dioscorides* calls it *erythrodanon*, and *Pliny rubia*. Its use for dyeing was expressly mentioned by both. In *Charlemagne's* "Capitularia" madder is mentioned as *varentia* or *varantia* (= *garance*), and its cultivation recommended. In the middle of the sixteenth century the cultivation of madder began in the Netherlands. *Charles V.* introduced it later on into Alsace, and *Bertin* into France. In Germany Silesia was the first country to cultivate madder, in the middle of the sixteenth century. In France and the Netherlands the madder industry attained great importance.

The reason why Turkey red dyeing became so important was the extraordinary fastness of the colour, which in this respect is surpassed by few other vegetable and even mineral colours. The alizarine obtained synthetically from anthracene being, however, of exactly the same chemical composition, and possessing the same qualities, has now almost entirely displaced madder.

Turmeric, Curcuma (*Gelbwurz*)

The root of the *Curcuma longa* and *C. rotunda*, plants growing in Asia, are brought on the market in lumps or as a yellow powder, and contain a yellow colouring matter, *curcumine*. It can be extracted by means of alcohol, ether, and alkalies, but less readily with water. The alkaline solution is brown. The colouring matter is sold in egg-shaped bulbs or flat cakes, is not fast to light or soap, and is used to a small extent for dyeing cotton, wool, and silk, solely because it is easy to work and requires no mordant to fix it on the fibre. In chemistry turmeric is used as a reagent and indicator. Its chemical composition has not been closely investigated.

Litmus (*Lacmus, Tournesol*)

Certain algæ (species of *Roccella* and *Lecanora*) found in the East Indies, South and Central America, and on the Canary Islands furnish a blue colouring matter, litmus (azolitmine, litum), containing various colouring principles, when treated with ammonia, alkali carbonates, and lime, and left to ferment. In the Netherlands the colouring matter is obtained from various algæ brought from Scandinavia and the coasts of the Mediterranean.

The plants are dried, ground, and mixed with ammonium carbonate, potash, and lime, the mixture being allowed to stand and ferment. The colour is violet at first, but after three weeks is perfectly blue. A further quantity of ammonia is added (gas liquor, stale urine), and finally chalk and gypsum. The mass is then pressed, formed into cubes, and dried. In the free state the litmus colouring matter is red, but in the state of saturated alkali salts it becomes blue.

The most important colouring principle of litmus is *azolitmin*.

Like turmeric, litmus serves especially as an indicator for chemical analysis, and is of no technical importance for dyeing. It is largely used in the Netherlands for colouring liqueurs, preserved fruit, confectionery, cheese, toilet articles, and sugar paper.

Lo-kao (*Chinese Green*)

From the bark, twigs, leaves, and the root of *Rhamnus utilis* and *R. chlorophorus* the Chinese prepare an aqueous extract, which, when treated with milk of lime, furnishes a green lake. It is largely used in China for dyeing cotton and silk, but not employed in Europe owing to its high price. The product comes on the market as thin, curved leaves of a dark green, somewhat violet-tinted colour. The dyeings are permanent.

Annatto (*Orlean, Anatto, Terra Orellana*)

This colouring matter is obtained from the red, fleshy covering of the seed of the rucca tree (*Bixa orellana*) inhabiting Central America, the Antilles, Cayenne, &c. In order to obtain the colouring principle the skinned fruits are thoroughly mashed with water and allowed to ferment for a fortnight, being afterwards passed through sieves. When the liquor has clarified, the red sediment is taken away, heated in large pans, and boiled down to a thick paste, which is made into cakes. It is sold either in a perfectly dry state or covered with leaves or rushes in boxes. The product is brown on the outside, but red inside.

There are two kinds on the market; the rarer, *East Indian* annatto, which is mostly sold in the dry state, is said to be the better of the two. The less valued annatto, from *South America*, called *orlean* (or Spanish), is soft, and easily rubbed down to powder. The fresh mass smells like carrots, but the commercial article sometimes smells strongly of ammonia, derived from the fermenting process or from the addition of urine, which is said to make the colour brighter.

Annatto is sometimes adulterated with mineral bodies, these being indicated when the product contains more than 10 per cent. of ash.

There are three colouring principles of a more or less red- to yellow-tone in annatto, the most important being *bixin*, $C_{28}H_{34}O_5$. A product found in the trade under the same name is five or six times stronger than ordinary annatto. The ordinary commercial product sometimes contains only 6 to 8 per cent. of colouring matter. Bixin is insoluble in water, but soluble in alcohol. The two other colouring matters dissolve in water, but are of no technical value.

Annatto is a substantive colouring matter for cotton, silk, and wool, and gives bright orange-red shades, fast to acids, soap, and chlorine, but not permanent in the light. For wool and silk dyeing annatto is seldom used, but is employed for colouring butter, cheese, margarine, &c.

Archil (*Orseille, Oricello, Orchilla*)

Archil, like litmus, is obtained from the algal genera *Roccella*, *Variolaria*, and *Lecanora*. It was first recognised as a dye-stuff at Florence in the fourteenth century, where archil dyeing was practised as a secret process. The consumption of archil afterwards made from numberless varieties of the above algæ, inhabiting not only the tropical zone, but also Scandinavia, &c.—was up to the nineteenth century very extensive, as it was used for a great many purposes.

To manufacture archil the plants are freed from adhering sand, stones, &c., thoroughly well mixed and worked with water, sometimes also boiled, and then passed through sieves. The colouring principles are now partly dissolved, and partly suspended in the water. The liquor is then treated with ammonia and gently heated. The colouring matter is precipitated as a paste, and is sold in that condition—archil in paste (*orseille en pâte*). According to another method, the finely ground algæ are first treated with soda, and afterwards boiled, the subsequent treatment being as above.

The colouring principle of archil is *orxeine*, $C_7H_8O_2$, which is developed by the oxygen of the air in the presence of lime and ammonia. In former times stale urine was also used.

If the archil paste is extracted with water and then carefully evaporated at low temperatures, another product, *archil extract*, or *archil carmine*, said to be twice as strong as archil, is obtained.

In Scotland an archil product is made, the so-called *persio*, or *cudbear* (red indigo), consisting of dried, ground, and bolted *Lecanora herpes*, indigenous to that country.

French purple, another archil product, is made by treating the algæ in the cold state with liquid ammonia, the filtered liquor being then treated with hydrochloric acid, and the resulting precipitate redissolved in ammonia. The solution is then exposed to the air in shallow pans. After a certain time the liquor assumes a cherry-red shade, turning to purple-red at about 75° C. The purple colouring matter, which has a violet shade, is precipitated with dilute sulphuric acid or tartaric acid. According to another method, the lime lake is precipitated from the ammoniacal solution by calcium chloride. The lime lake is also sold as French purple.

These two articles were at one time largely used for dyeing wool red and violet, and to a smaller extent for silk. Pure French purple was decomposed in ammoniacal solution, the lime lake with sulphuric acid, and the colouring matter dissolved in ammonia was dyed directly on the wool. Orceine is therefore a substantive dye-stuff.

Pure *orceine* is obtained from the artificial archil by acidifying it with hydrochloric acid and evaporating it to dryness. The residue is boiled with alcohol, evaporated to dryness, and then washed with water and ether. Orceine obtained in this way is a carmine-red powder.

The archil dyeings are very bright, violet and bluish red, and are very uniform on the stuff, but as a rule are not permanent, only the French purple giving fairly fast shades. Archil is now displaced by coal-tar colours, so that the import trade has considerably decreased.

The most suitable species of algæ occur in Ceylon, Madagascar, Mozambique, and Zanzibar, and are called *herb-archil*. They are purer than the so-called *earth archil*, the latter being generally the raw material for making litmus. In the chemical treatment of the plant for recovering the archil colouring matter *orcine* is formed at first as a decomposition product of the algic acids, and is converted into *orceine* by the action of ammonia and air, a red crystalline colouring matter being produced.

The value of archil preparations is determined, according to *von Cochenhausen*, by a dyeing test. 5 grms. of the archil to be tested are dissolved in 1 litre of water, and 50 c.c. of the solution are dyed on 1 grm. of wool. The dye-bath is made up with 10 per cent. (taken on the weight of the wool) of alum, and 2 per cent. of tartaric acid are added, the dyed wool being then compared with the standard types, dyed under the same conditions.

For the determination of the algic acids, containing the colouring matters of the plant, 100 grms of the ground plant are twice extracted, hot, with dilute caustic soda. The solution is oxidised by the aid of a solution of sodium hydrochlorite of known strength, run in from a burette, until the originally dark red solution is changed to a pure yellow shade. Archil is adulterated with logwood, or red wood extract, or with magenta.

Quercitron

Quercitron is the dried ground bark of certain species of oak, *Quercus tinctoria* (*nigra*), *Q. digitata*, *Q. trifida*, inhabiting North America (Pennsylvania, Georgia, Carolina), which were formerly also cultivated in Europe, especially in France. Quercitron comes into the market as a powder, and as an extract of about 10° to 20° B. strength. The extract readily deposits crystals, and is a good habitat for micro organisms; it must be stored under special precautions. The colouring principles of quercitron are *quercitin* and *quercitrin*. The latter is the glucoside of the former—viz., of the real colouring principle.

Quercitrin, $C_{21}H_{22}O_{12}+2H_2O$, is obtained by boiling the bark for six hours with a fivefold quantity of 85 per cent. alcohol. Half of the alcohol is distilled off, and the solution is treated with strong acetic acid, followed by an alcoholic solution of lead acetate to precipitate the impurities. Any excess of lead acetate must be avoided. The liquid is filtered, and treated with sulphuretted hydrogen to precipitate the lead. It is then evaporated to dryness, the residue, *quercitrin*, is dissolved in alcohol, reprecipitated with cold water, and repeatedly crystallised from boiling water. The resulting pure quercitrin forms slightly yellow, brilliant, fine needles and scales; it is insoluble in cold water and ether, but soluble in hot water, alcohol, or strong acetic acid.

Quercitrin has a much lower tinctorial power than quercitin

When quercitrin is boiled for some hours in water, very slightly acidified with sulphuric acid, a lemon-yellow powder, *quercitin*, $C_{15}H_{10}O_7$, is precipitated. It is very slightly soluble in hot water, and nearly insoluble in cold water. Hot alcohol also dissolves it better than cold.

Quercitin is formed from quercitrin in accordance with the following equation:

$$\underbrace{C_{21}H_{22}O_{12}}_{\text{Quercitrin}} + H_2O = \underbrace{C_{15}H_{10}O_7}_{\text{Quercitin}} + \underbrace{C_6H_{14}O_6}_{\text{Isodulcite.}}$$

Isodulcite is a kind of sugar which can be obtained in a crystalline form, and is identical with the sugar (rhamnose or rhamnodulcite) formed by the decomposition of xanthorhamnin, the glucoside of rhamnine (see "Persian berries"), and there called rhamnose or rhamnodulcite.

The quercitron preparations are used for dyeing and printing cotton, and to a small extent for dyeing silk and wool. They give various shades with different mordants—with tin a bright orange, with chromium a brown orange, with alumina a yellow brown, and with iron a dark olive. Quercitron serves chiefly for shading other colours, and is rarely used alone for dyeing. The dyes are only moderately fast to light, having a tendency to darken. They will stand milling fairly well.

Another quercitron product, brought into the trade from America, and now largely used, is *Flavine*, a dark grey-yellow to brownish powder. It contains nearly pure quercitin, but only very little quercitrin, and is manufactured by preparing an extract from quercitron bark by boiling it with a solution of soda, and the alkaline solution is slightly acidified with sulphuric acid. On applying gentle heat the flavine is precipitated. Its tinctorial power is sixteen times that of quercitron.

Quercitin is also found in various other plants besides those mentioned; for instance, in the flowers and fruits of the chestnut, in buckwheat, gilly-flowers, blackthorn, &c., though only in small quantities, and of no technical importance.

In testing quercitron bark the chief points are a pale yellow colour and a fairly low content of water and ash. The extracts are adulterated with gelatin and dextrin, flavine especially with yellow wood bark and calcined Glauber salt. Pure flavine gives in boiling water a cloudy, pale greyish-yellow solution. On addition of aluminium sulphate the solution should be bright yellow in colour, without any precipitate. A solution of flavine loses its tinctorial power when left for some time in an open vessel.

The colouring power is determined by trial dyeings as already described. 10 grms. of quercitron extract, or the corresponding quantity of bark or flavine, are dissolved in 1 litre of water, and 20 c.c. of the solution used to dye 1 grm. of wool. The latter must be prepared beforehand with a mordant of 1·5 per cent of tin salt and 3 per cent. of oxalic acid. A series of standard types are kept for comparison.

Redwood, Brazil Wood (*Rotholz, bois rouge*)

Redwood is a collective name applied to a large number of various species of wood, belonging, like logwood, to the family Leguminosæ, genus *Cæsalpinia*, and found in the East Indies, South and Central America, the Antilles, Africa, Jamaica, and the Bahama Islands The following principal kinds are known: *Fernambuco*, or *Pernambuco wood*, the most valued kind, comes from Brazil and Jamaica as large, round, very hard baulks, shipped from Pernambuco. The wood is red in colour, yellow when newly cut, but soon darkening. *Bahia* or *Brazil wood* is shipped *via* Bahia, and is of lower tinctorial power. It comes on the market in squared logs. *St. Martha* (*Marton*) *wood* comes from Mexico in logs weighing about 35 lbs., and is less appreciated than Fernambuco wood. *Nicaragua wood* is in the form of unbarked branches as thick as a man's arm. *Sapan* or *Japan wood*, hard, red, barked logs, but with yellow pith, sometimes with empty pith-channel, is also called "false sandal wood," and comes from Siam, China, Japan, Cochin China, Celebes, Java, the West Indies, the Antilles, &c. It is a good brand, of about the same value as Fernambuco wood. *Lima wood* comes from South and Central America in logs about 1 ft. thick; *Brasiliette*, *Jamaica*, and *Bahama redwood* are poorer brands from a bush (*Balsamodendron*) growing in the Antilles, Bahama, Guiana, &c., and shipped in peeled lengths about 2 ins. thick, with a whitish skin. The *California wood* brands come from California, twined in tresses, and soon darken in the air. *Terrafirma wood* is imported from Colombia.

A similar great variety exists with regard to the different shades that can be obtained from the various brands of redwood.

Redwood extracts are prepared in the same manner as already mentioned in the case of logwood extract.

In this wood also the colouring matter is not contained in a developed state, but only in the form of a compound rich in hydrogen, viz., *brasilin*, $C_{16}H_{14}O_5$, which, when carefully oxidised, furnishes the red colouring matter *brasilein*, $C_{16}H_{12}O_5$.

Brasilin is prepared from redwood extracts by various methods. *Chevreul* evaporated the decoction to dryness, extracting the residue with alcohol, diluting the concentrated solution with water, and finally precipitating the tannic acid with a solution of glue. The filtrate was again concentrated, and the brasilin taken up with boiling alcohol, from which it crystallised out on cooling.

According to *Bolley* and *Kopp*, the red incrustations deposited from red wood extract after a certain time, and containing brasilin compounds, are preferably used. These deposits are triturated with dilute acids, washed, and the residue extracted with water and a little alcohol, The brasilin crystallises from the filtrate in felted yellow needles, and can be obtained from dilute solutions in tablets with variable content of water (1 to 1½ molecules). The crystals turn red in the light, have a bitter-sweet taste, and are soluble in water, alcohol, and ether. The solutions also turn red in the air. Brasilin gives a carmine-red solution with dilute caustic soda, losing its colour when heated with zinc dust on the water-bath with exclusion of air. In presence of the slightest trace of oxygen the red colour reappears.

To obtain *brasilein* from brasilin, the above-mentioned alkaline brasilin solution can be used after standing two to three days. On adding an excess of acid the colouring matter settles down on cooling as an amorphous red-violet mass, with a golden tinge.

According to *Buchka* and *Erck*, a solution of 10 grms. of brasilin in a little alcohol and 400 grms. of ether is oxidised with 5 grms. of strong nitric acid. The mass is allowed to remain therein an hour and a half, and two-thirds of the ether are then distilled off, the rest of the solution being allowed to evaporate in the air. The brasilein settles down in the form of lustrous plates.

If air be led through a dilute alkaline solution of brasilin, previously treated with alum, a brasilein lake is deposited in the form of a powder or as a paste when the mixture is acidified. Zinc or chromium lakes can be obtained in the same way.

Redwood was formerly very largely used, but now very little, as it is only employed in cotton dyeing and printing to produce mixed shades. It is also occasionally used for dyeing wool.

Redwood dyes are not fast to light or soap, and are destroyed by acids and alkalies—reasons sufficient to explain their almost complete abandonment for dyeing.

Redwood was used in the earliest times in East India as a dye; and as far back as 1190 dye-woods called brazil (from *braza* = red heat) were mentioned. On the discovery of South America in 1500 the country of Brazil is said to have received its name on account of this dye-wood being found there in large quantities.

As a substitute for redwood a dark yellow-red wood, obtained from a cotton plant, *Baphia nitida*, is brought into the trade from the west coast of Africa (Sierra Leone, Liberia) or Jamaica. It is called *cambal wood*. The aqueous extract is of a yellow-red colour, turning to orange on addition of lead salts. The cambal wood dyes are said to be less brilliant, but considerably faster, than the ordinary redwood dyes. The lakes prepared from redwood are now rarely used.

Safflower (*Safflor, Carthame, Safran Bâtard*)

Safflower is the dried petals of *Carthamus tinctorius*, growing in some parts of Asia, and now cultivated in nearly all countries, especially in Spain, Italy, Germany, Hungary, Russia, Persia, Mexico, South America, and Egypt. Two kinds of safflower are known—one with large petals, the other with small ones, the latter coming chiefly from Egypt.

A whole series of different brands are known in the trade. The dark red *Persian safflower* is considered the best, *Egyptian* or *Levantine safflower* coming next. Other brands are the *East Indian, the South American, Spanish, Hungarian* (from the neighbourhood of Debreczin), *Italian, Russian,* and *German safflower,* from Thuringia and the Palatinate.

Safflower is an annual, blossoming in July and August. The flowers are collected as they fade and dried in the shade, or worked up with water into small balls, or, finally—as is done with Argentine safflower—steeped in salt water, kneaded, pressed, and finally dried. The latter method is specially designed to remove a worthless yellow colouring matter from the safflower and to diminish the weight.

A good brand of safflower is free from calices and foreign bodies of mineral origin. It should feel soft, somewhat damp, be delicate in fibre, cohesive, of a dark bright red colour and strong aroma. If the flowers have been gathered too late or not properly dried the colour is pale.

Safflower contains two colouring principles *safflower yellow*, which is almost entirely soluble in water, and *safflower red*, or *carthamine*, sparingly soluble in water. The yellow colouring matter is present to the extent of about 30 to 36 per cent., carthamine only 0·3 to 0·5 per cent. For dyeing the Carthamine alone has to be considered, safflower yellow being of no practical value. This also affords a reason for the special treatment applied by the Egyptians, as mentioned above. According to others, safflower is said to contain two yellow colouring matters (besides the red one), one of which is an acid (27 to 30 per cent.) and soluble in cold water, the other (2 to 6 per cent.) being only soluble in alkaline water. The colouring matters have not yet been obtained sufficiently pure for special investigation.

According to *Schlieper, carthamine* is manufactured in the following way:

Safflower is washed for some time with water to remove the yellow colouring matter as much as possible. The remainder is then treated with a weak solution of soda and pressed, the solution then containing the carthamine and various other constituents of the plant. To eliminate these impurities it is dyed on cotton, strips of which are dipped in the alkaline solution and treated with acetic or citric acid to liberate the carthamine, which is then precipitated on the strips, and colours them dark red. The strips are next washed, and treated again with a solution of soda which dissolves out the colouring matter. The dark red alkaline solution is treated with acids, whereupon a flocculent carmine-red precipitate of pure carthamine comes down. This is filtered and washed, treated with alcohol, and (after the bulk of this latter has been distilled off) is finally evaporated over sulphuric acid *in vacuo*. Carthamine then forms dark red crusts with a greenish sheen, or a greenish-black powder. It is sparingly soluble in water and ether, but readily soluble in alcohol.

Safflower yellow is not recovered from the leaves. It decomposes very easily and quickly, especially in aqueous solutions.

There are various brands of safflower on the market, partly used for dyeing, for painter's colours, and especially for the manufacture of toilet articles. Safflower red is also used for this latter purpose, as well as in the manufacture of artificial flowers, liqueurs, confectionery, &c.

An impure carthamine, the so-called *vegetable red* (*rouge végétal*), is got up for sale by drying it on cards, cups, plates, &c. (*rouge en assiettes, en tasses, en feuilles*). *Safflower carmine* is a strong, viscous solution of carthamine in water containing soda, and was formerly used for dyeing.

Safflower red, therefore, is difficult to obtain even in merely small quantities, and is consequently rather dear, and is not at all permanent as a dye.

The colouring matter fades very quickly under the influence of a weak solution of soda or other alkalies, chlorine, sulphurous acid, and in sunlight. This explains why safflower has been almost entirely displaced by artificial colouring matters.

It may be mentioned here that roasted cobalt ores, intermediate products in the manufacture of smalt and other cobalt pigments, are also called safflower.

Saffron, Crocus (*Safran*)

The saffron plant, *Crocus sativus*, comes from the Orient, but was also formerly cultivated in the South of France, in Spain, Austria, Switzerland, and North Africa. Even now it is grown to some extent as a colouring ingredient for cakes, &c. The flowers are dried, and furnish a dark reddish-yellow powder with a strong aromatic smell. Besides *saffron oil* and a *bitter principle*, the product contains the colouring matter, *crocin*, in the form of a glucoside.

To manufacture *crocin* in the pure state, the saffron oil is removed by agitation with ether, and the colouring matter then extracted with water. The aqueous solution is shaken up with freshly burned bone black, which entirely removes the colouring matter, but gives it up again when shaken with alcohol. The resulting crocin forms a brittle, yellowish-brown mass, soluble in water and dilute alcohol, more sparingly in strong alcohol, and insoluble in ether.

Saffron is now only used for colouring confectionery.

Sap Green

This name is given to an inspissated extract of unripe buckthorn berries, to which some indigo carmine and alum have been added. It is not very permanent, and has only very little practical value.

Santal Wood

This wood is obtained from large trees, *Pterocarpus santalinus* and *P. indicus*, growing in the East Indies, Ceylon, Timor, and on the Coromandel coast. It comes on the market in squared logs, is extraordinarily hard and heavy (sp. gr. 1·014), and contains about 16 per cent. of a colouring matter, *santalin*.

For the manufacture of santalin the ground wood is extracted with ether, the greater part of which is then evaporated, whereupon crystals of impure santalin are deposited. Santalin is then precipitated from the alcoholic solution of these crystals by lead acetate, as a lead salt (santalin has acid properties, and is therefore sometimes called santalic acid), which is boiled with alcohol and decomposed with sulphuric acid. The solution is separated from the lead sulphate and concentrated, the santalin separating out as small red crystals, melting at 104° C. Santalin is sparingly soluble in water, but readily soluble, to a blood-red solution, in alcohol, ether, and acetic acid.

The ground santal wood is used direct for dyeing cotton and wool, the colouring matter being developed on the fibre by the aid of various mordants, and furnishing Bordeaux-red to blood-red shades. The santal wood dyes being, however, very fugitive in the light, they are no longer used for cloth dyeing, but only for colouring confectionery, liqueurs, and tinctures.

Woad (*Luteolin, Wau*)

This is derived from a species of *Reseda*, *R. luteola*, growing in Central Europe (Germany, England, France), and formerly cultivated to some extent. The one-year-old plants are collected and dried in the air, and contain (especially in the flowers) the colouring matter *luteolin*.

Luteolin, $C_{15}H_{10}O_6$, is recovered from the aqueous extract of *Reseda luteola*. Dry extract is boiled for some hours with water acidified with hydrochloric acid, then filtered through cloth to separate the precipitated resin from the solution, and allowed to stand for a day. Brown impure luteolin is formed, which is filtered, washed, and dissolved in ether, the resulting emulsion being strained through cloth. The ethereal solution is shaken up with a dilute alkali, and on acidifying the latter the colouring matter is thrown down, and is dried. If the colouring matter is again treated with hot alcohol, a yellow crystalline mass is formed on cooling, and this furnishes quadratic yellow crystals in the shape of regular concentric needles when recrystallised from alcohol. The needles melt and sublime, with partial decomposition, at 320° C. They are sparingly soluble in boiling water, very slightly so in cold water, but more readily soluble in alcohol. Solutions of alkalies, alkali carbonates, and ammonia dissolve luteolin to a deep yellow solution. On evaporating the ammonia pure luteolin is left behind. Strong sulphuric acid gives a dark reddish yellow solution.

Woad is used for dyeing cotton and wool, yellow, brownish, and olive shades being obtained, which, however, are not fast to light or soap. The alumina lake, however, dyes silk a bright and permanent yellow, and is still used occasionally.

Waras

The husks of a bushy plant, *Flemingia congesta*, growing in India and Africa, contain a red resinous powder, which in the dry state forms the colour drug *waras*.

Waras is extracted with carbon disulphide, dried, and afterwards treated with hot chloroform for some time, the liquid depositing a red precipitate on standing. The precipitate is separated from the liquor by filtration, and the filtrate is evaporated. The residue is crystallised by means of toluene, and gives an orange-red crystalline powder, *flemingine*, $C_{12}H_{12}O_3$. It is readily soluble in alcohol and acetic acid, but sparingly soluble in toluene and chloroform, and melts at 171° C. The red precipitate obtained by the chloroform treatment is crystallised again from hot chloroform, and furnishes a red resin. *Homoflemingine* remains in solution, and can be obtained, by evaporating the liquid, as fine yellow needles, melting at 165° C. It seems to have the same chemical composition as flemingine.

Waras is mainly a dye for silk. The operation is performed in a boiling solution of soda, and furnishes golden yellow shades with an orange tinge.

Wongshy (*Wongs-hy*)

The fruit of a plant, *Gardenia grandiflora*, growing in China, yields a colouring matter which has been isolated as an amorphous red body, and is believed to be identical with the crocin obtained from saffron. It is used in China for dyeing cotton, and produces green and yellow shades.

We have now dealt with the most important animal and vegetable colouring matters, especially those formerly used to a considerable extent and still partly employed. No attempt has been made to give an exhaustive description of all known vegetable colouring matters, or to explain their chemical constitution, &c. A purely practical work like the present is bound to confine itself to the requirements of existing practice, which is not largely concerned with more than a few of the natural organic colouring matters; these will be more fully treated in the manufacturing section.

PART II

ARTIFICIAL ORGANIC COLOURING MATTERS

COAL-TAR COLOURS

The origin and development of the coal-tar colour industry represent one of the greatest triumphs of modern chemistry during the last century. In spite of the short period (half a century) that has elapsed since the manufacture of these products was commenced on proper lines, the number of the manufactured products is now so great, their application so varied, and consequently the demand so immense, that, in Germany especially, very extensive works, occupying many thousand hands, are now engaged in the manufacture of these products, a still larger number of persons being concerned with the commercial side of the industry.

The manufacture of the first known artificial organic colouring matters was roughly coincident with the beginning of the scientific study of organic chemistry, which originated in the investigation of pharmaceutical and medicinal remedies.

The earliest of the artificial organic colouring matters made their appearance in the eighteenth century. *Welter* discovered *picric acid* by treating certain resins with nitric acid, and it is remarkable that this first artificial organic colouring matter still retains its importance. By treating uric acid with nitric acid *Scheele* obtained *murexide*, which was temporarily used for dyeing purposes. These discoveries, however, were not the beginning of really scientific studies in colour chemistry, but were merely accidental, and not arrived at by design. In order to enable a rational and systematic study of the manufacture of technically suitable colours to be pursued, it was primarily essential to have at disposal a sufficient quantity of raw material at a suitable price. This material was found in coal tar, which at the beginning of the coal-gas industry was a by-product of no value. The quantities of tar obtained, however, were so great as to render the discovery of some method of utilising them a pressing necessity. The preservative power of the tar as a coating for wood was recognised, and another use was discovered for it as fuel.

Tar is a distillation product of coal and lignite, the chemist applying the term "dry distillation" to the process of decomposing dry organic bodies in a retort. Coal is a vegetable product. While the plant lives it takes up food from the earth, and works it up by the aid of light and heat from the sun. The dead vegetable substance gradually loses all its oxygen and becomes richer in carbon, until it ceases to resemble an organic body, and assumes a more and more decidedly mineral character. According to the age and degree of this process of decomposition—*i.e.*, with reference to the termination of the carbonising process—the fossil development of dead plants can be classified as follows: peat, lignite, and coal, the latter in its purest state forming anthracite.

Just as modern physiological chemistry is quite able to recognise and control the vital activity in all parts of plants, so also can it utilise all the products of this metabolism. Warmth and light, which enable the plant to live, are stored up in the plant in a latent condition; and coal must therefore be regarded as an accumulator of heat that can be utilised in different ways. Colour, however, is a product of light; and the light which once illuminated the plants can also be considered as warehoused in the coal, so that the colours of the plants fossilised during thousands of years are now recovered in new beauty by chemical science.

Coal is decomposed by dry distillation into gases and liquids, which are collected separately. The liquid chiefly consist of water and tar, this latter forming an extraordinarily complex mixture of various bodies. *Runge* and *Reichenbach* were among the first to investigate tar. Runge studied coal tar, and isolated *phenol* (carbolic acid) and *cyanol* (aniline), together with a colouring matter, *rosolic acid*. Reichenbach found in wood tar *creosote* and *paraffin*, and also a colouring matter, *pittacall*; but these discoveries at first excited little attention. *A. W. Hofmann* was one of the chief founders of the coal-tar colour industry, his researches first revealing the compounds on which the coal-tar colour industry is still based. Hofmann found that Runge's *cyanol*, Unverdorben's *crystallin* (obtained by distilling indigo), Zinin's *benzidam*, and Fritzsche's *aniline* were all the same body—viz., *amidobenzene-aniline*. He also found that the benzene obtained by *Mitscherlich* from benzoic acid is contained in coal tar. *Mitscherlich* had shown how to transform benzene into the nitro derivative; and *Zinin* obtained amidobenzene from nitrobenzene and called it *aniline*. The composition and relation of these bodies one to another and towards phenol, benzaldehyde, &c., were ascertained, these bodies were manufactured, and a commencement was made to use coal tar instead of vegetable products as the raw material for them (1845).

In 1849 *picric acid*, already long known, was practically applied in dyeing, *Guinon* (Lyons, 1849) using a patented process for dyeing silk yellow with picric acid. Finally, in 1856 the first true aniline colour, "Perkin's violet," was discovered by the English chemist *Perkin*, who prepared it from aniline by means of potassium bichromate.

Perkin found this colouring matter possessed hitherto unknown tinctorial power and brightness, and he himself utilised the discovery: practically *he established the first manufactory of coal-tar colours*. Perkin's violet was sold as *mauvein*, or *mauve* (after the violet flowers of the mallow).

After this most important discovery of beautiful violet from colourless aniline, a great many chemists tried (and successfully) to prepare it from the same material by another method than that used by Perkin. *Caro* obtained the same body by the aid of cupric chloride, *Scheurer-Kestner* with bleaching powder. Moreover, similar investigations were made in many other directions. *A. W. Hofmann* and *Nathanson* had already in 1858 by treating aniline in various ways obtained a bright red body, which was obtained again in 1859 by the French chemist *Verguin* in a different manner. A French house took out a patent for manufacturing this colouring matter, which was found to be of even greater value than mauvein ; and the product was brought into the trade as *magenta* (fuchsine). Hofmann, after studying the green, fluorescent crystals, found them to consist of a salt of an organic base, which he called *rosaniline*—a substance colourless in the free state, though forming coloured salts. He also discovered that rosaniline cannot be made from pure aniline, but that it is produced from toluidine, a body associated with aniline.

Rosaniline base was also studied by numerous chemists. By various methods *Hofmann* and *Geyer* obtained *Hofmann's violet ; Nicholson* a blue colouring matter ; *Cherpin* and *Usèbe* a green, which was soon followed by another green colouring matter, *methyl green ;* so that all the colours of the spectrum, except yellow, were obtained from rosaniline.

A colouring matter of different origin was Lauth's *methyl violet* (from which *methyl green* can be obtained); another being *aurine* (*Kolbe and Schmidt*). The latter is homologous with *Runge's rosolic acid.*

Lightfood (1863) found *aniline black* a colouring matter of the greatest importance for dyeing and printing.

Up to this time the activity of chemists in this new branch of colour chemistry had been of an empiric character, but *Kekulé's* theory of the constitution of benzene (1867) brought a sudden change, and chemists tried to produce the various derivatives and substitution products revealed as possible by this theory, their experiments proving highly beneficial to the colour industry.

The artificial production of *alizarine* (1868 and 1869), the well-known colouring principle of madder, from *anthracene* by *Graebe* and *Liebermann* was of the highest importance. (Anthracene is similar to naphthalene, and is also present in coal tar.) Their method of producing alizarine, however, was unsuitable for manufacturing purposes, the product being too dear ; but it indicated the proper way, and soon afterwards *Caro* and *Perkin*, working on different lines, found a practicable process. The synthetic manufacture of alizarine naturally had serious economic results in the countries where madder was cultivated on a large scale, affording profitable employment to a large number of people and large returns to the revenue. The conditions of two hundred years previous, when the existence of the woad cultivators was threatened, were repeated. Attempts were made to restrict the importation of alizarine by means of premiums to the madder cultivation and grants, but with the same negative success as in the case of indigo. This struggle against alizarine was perhaps the reason why the coal-tar colour industry, which, as already seen, was originally centred in France and England, has been transferred to Germany, this step being also assisted by certain legislative advantages granted in the latter country. In the first place, the absence of any patent law enabled foreign inventions to be worked, and there was no tax on alcohol for chemical purposes—advantages not so fully shared by England and France.

In addition to the red, a number of blue and other colours, distinguished by great permanence, were soon obtained from alizarine.

Binitronaphtol, the first naphthalene colouring matter, and closely allied to picric acid, was prepared by *Martius*, the same raw material also furnishing the bright red colouring matter *Magdala red.*

Baeyer in 1874 discovered quite a new class of colouring matters with *acid* properties, the *phtaleines*, all those previously known being of a *basic* character. The first of this class was a bright red, which exhibited a strong greenish fluorescence in alkaline solutions, and was therefore called *fluorescein* (*Baeyer*).

Caro, by treating fluorescein with bromine, obtained the famous *eosine*, which was followed by a number of variants obtained by similar reactions. A species of phtalein, *rhodamine*, discovered in 1889 by *Cereosole*, is a colouring matter as bright as eosine, but much faster.

E. and *O. Fischer* in 1877 discovered *malachite green*, which is still manufactured from benzaldehyde by their method. *Lauth* obtained in 1876 *chinonimide*, containing sulphur, from which class *methyl violet*, and later on *methylene blue*, were derived by *Caro*. At the same time *chrysoidin* and the important class of *azo colours* were found, and were specially investigated by *Kekulé* and *Hidegh*; and *oxyazo compounds*, from which *P. Griess* obtained *diazo compounds*. *O. N. Witt* and *Roussin*, a French chemist, made a special study of the azo colours, a group which, in point of variety of colours, applications, and extent of manufacture, has attained much greater importance than any other. Azo colours may be of acid or basic character, and either adjective colours or developed on the base or fibre.

At the end of the nineteenth century, after twenty-five years' strenuous labour, *indigo*, the most important colouring matter, and one known and used from the earliest times, was prepared *synthetically*. Already in 1869 *Baeyer* and *Emmerling* had discovered *indol*, and *Nencki* had obtained indigo blue by the oxidation of this substance. *Engler* and *Emmerling*, and also *Claisen* and *Shadwell*, prepared synthetical indigo in various ways; but their methods were of merely scientific interest, and could not be applied in practice. In 1880 *Baeyer* applied for a patent for his methods of manufacturing artificial indigo. *Baeyer* himself, and other workers like *Heumann*, *Hoogewerff* and *van Dorp*, *Sandmeyer*, and others, extended and perfected the original methods and discovered new ways of manufacturing indigo synthetically.

The manufacture of artificial indigo continued to make progress, and by 1900 the Badische Anilin- und Soda-fabrik, of Ludwigshafen, was already producing about 1000 tons of artificial indigo—a quantity equal to about one-fifth of the total production of natural indigo. The manufacture of synthetical indigo having now been taken up by the Höchst Farbwerke and other colour-makers, the natural indigo industry will soon meet the same fate as the madder industry. This change, however, will really benefit those countries where indigo is now cultivated, since the immense tracts of land devoted to this purpose—and from which the natives derive less profit than foreign capitalists—can then be used for growing wheat and other food-stuffs.

Mention should also be made of the *sulfine colouring matters* (coal-tar colours containing much sulphur), of recent date, but of the greatest importance. In 1873 *Croissant and Bretonnière* obtained colouring matters by fusing various organic bodies like tannin, cotton, wool, silk, glue, starch, sawdust, &c., with sulphur, or sulphur and caustic soda (alkali sulphides). These colouring matters, containing sulphur, are capable of dyeing the vegetable fibre direct, and furnish very fast dark grey to black shades, especially when afterwards treated with potassium bichromate. In spite of the bad smell of the contained mercaptan compounds, these colouring matters (known as *sulfine colours* and *cachou de Laval*) were largely used in England, France, and Italy. They are soluble in alkali sulphites, and in this condition are sold as *cachou de Laval S.*

After a long interval *Vidal* reinvestigated these colours, and by treating derivatives of the aromatic series obtained (in 1893) a group of bright black fast colouring matters, which he called *noir Vidal*, or *thiocatechin*, and patented. Vidal's work led to a thorough investigation of these colours, and a large number of manufacturing processes were devised. Sulfine colours of special value* are *immedial black* (Cassella) and *Katigen black* (Elberfeld).

In this review of the most important periods in the progress of the coal-tar colour industry we must include a short history of its development, which, for Germany especially, was of the highest importance. In no other branch of chemical industry have practice and science been so intimately combined as in the manufacture of artificial colouring matters, and no other industry has fostered and enriched chemical science to such a degree. The scientific colour chemists cannot and must not work empirically. The material at disposal is thoroughly investigated, its constitution and properties are known, tests and reactions are performed in accordance with a definite scientific plan and for the attainment of theoretical ends; and it is only very seldom that the colour chemist meets with substances and products within his province with the chemistry of which he is not acquainted.

COAL TAR: ITS MANUFACTURE AND TREATMENT, AND THE RECOVERY OF INTERMEDIATE PRODUCTS

a. The Raw Material

It has already been mentioned that the coal-tar colour industry was not founded in Germany, but in England and France; and it was especially pointed out that the proper investigation of the derivatives suitable for dyeing purposes did not become possible until a cheap raw material was at disposal in large quantities, instead of merely vegetable products found in small quantities and only at certain seasons. Such a material is coal tar, a by-product of the manufacture of coal gas, which was used for illuminating purposes in England and France much earlier than in Germany.

Sources of natural gas issuing from the earth have been known from the earliest times, and such gas was also used for illuminating purposes. *Becher* (Munich, 1682) and *Hales* (1727, England) studied the decomposition of coal by dry distillation, and showed that a combustible gas was produced. *Clayton* and *Minkelers* in 1784 continued these researches, and their results induced *Lord Dundonald* to pass the gas produced in his coke furnaces at Culross Abbey through coolers and then collect it. He separated the gas from the liquid distillation products, and used the former for lighting his works. The Scotch engineer *Murdoch* established plants for lighting factories with coal gas at various places; and the German *Winzler* (in association with *Clegg*, a Scotchman) lighted a street in 1808, and later on the whole parish of St. Margaret's, London, by gas (1814), both in the streets and houses. *Clegg* had already devised apparatus for purifying gas with milk of lime, as well as the gas meter, and these two engineers established a regular gas factory. *Winzler* (1817) also introduced gas-lighting in France. In Germany gas-lighting was introduced at Berlin and Hanover in 1827, at Dresden and Frankfort-on-Main in 1828, the plant being supplied by English companies.

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* The manufacture of sulfine colours has recently made an extraordinary advance. In 1906 all shades were known except a bright red. In 1907 the Kalle colour works at Biebrich-on-Rhine discovered *thioindigo red* and *thioindigo scarlet*, two red colouring matters of the highest importance, being very fast to acids and also chlorine. [TRANSLATOR.]

The manufacture of coal gas forms, so to speak, the mother industry of the coal-tar colour industry, and from what has been said it is very easy to see that England and France were the likeliest places for the development of coal-tar colour-making. Conditions, however, have now entirely changed. At first the German coal-tar colour industry depended on English gas for its supply of raw material, and large quantities of tar products were imported into Germany for colour-manufacturing purposes. At present German iron-masters collect the tar produced in the blast furnaces and coking plants, and, with this source in addition to gasworks tar, the German coal-tar colour industry has become independent of foreign countries. In fact, despite the immense extension of the industry, it is now unable to consume more than a portion of the tar products available.

The coal used for gas-making and coking is mined in Germany in Rhenish Westphalia (the so-called Ruhr coalfield), on the Saar, in Silesia, and also in Saxony (near Zwickau, Chemnitz, and Plauen), and in Bavaria (Stockheim). England, Belgium, and France, and latterly Australia too, send gas coal to Germany in considerable quantities, especially to the North German ports. The Austrian gas coal mined at Pilsen and Ostrau have also to be taken into account.

The dry distillation of coal furnishes gas, ammonia liquor, tar, and coke. The quantity of these products varies, and depends on the nature of the coal used, the temperature and duration of the process, the size of the charge, and the pressure obtaining in the retorts. Tar being the only product of interest here, there is no need to discuss the rest.

Coal tar is a brownish-black, oily, viscous fluid, coloured by suspended carbon, and of an exceedingly complex composition. This varies not only according to the coal distilled, but the tar from one and the same coal will vary according to the way the distillation is conducted. Lignite, wood, and peat contain much hydrogen and oxygen, and hence the tar from these materials is of different composition than that from coal containing little hydrogen but much carbon. Lignite yields tar especially rich in derivatives of the fatty series, whilst coal tar furnishes the aromatic bodies required by the colour industry. Tar from coke ovens is less uniform in composition, and is only of value for colour-making when produced at high temperatures.

A ton of coal distilled in gas retorts yields about 1 cwt. of tar, of sp. gr. 1·1 to 1·26.

Tar contains more than a hundred distinct substances, more or less accurately known and identified.

To separate and isolate these the tar is redistilled, furnishing gaseous, aqueous, and oily distillates, the last-named setting more or less hard when cold, whilst pitch remains as a residue in the retort. Tar distilling is now a separate industry, the tar being subjected to "fractional distillation" in large stills or retorts (about 10 ft. wide and 12 ft. high), the various fractions of the distillates being collected separately, according to their temperatures. The water occasionally present in the tar distils over with the first runnings, up to about 110° C., and is followed by the "light oils," up to 170° C. Next the "medium oils" pass over until 230° C. is reached, then the "heavy oils" (270° C.), and finally anthracene (green oil), which is collected as long as any distillate comes over. In the most recent practice the distillation is assisted by reducing the pressure in the stills or by means of superheated steam, especially towards the end of the process, the distillates then being no longer liquid, but solid, at the ordinary temperature, though kept in a liquid state by the hot steam. For the same reason the pipes in the condenser are heated with water or steam instead of being cooled, or the distilled products would condense and choke the pipes.

The oily distillation products, which alone are valuable to the colour manufacturer, form about 48 per cent. of the total distillates, and contain, *inter alia*, the following bodies, in percentages of the original weight of coal-tar: *Benzene*, 0·6 to 0·8 per cent.; *toluene*, 0·2 to 0·4 per cent.; *xylene*, 0·1 to 0·2 per cent.; *phenols*, 0·2 to 0·3 per cent.; *cresols*, 0·5 to 0·8 per cent.; *naphthalene*, 2 to 10 per cent.; *anthracene*, 0·2 to 0·4 per cent. These compounds form the raw material for the manufacture of artificial organic colours.

Besides the above-named compounds, tar also contains cyanogen, nitrogen, carbonic acid, hydrocyanic acid, sulphuretted hydrogen, ammonia, methane, ethane, acetylene, and other derivatives of the fatty series, phenanthrene, fluorene, pyrene, chrysene; also chinaldine, aniline, lutidine, acridine, carbazol, &c.

The crude fractions from the first distillation are subjected to further treatment, and the resulting material is purified. The benzenes are washed with sulphuric acid and neutralised by alkali; naphthalene and anthracene are freed from adherent oils by hot and cold pressure, and sublimed if necessary.

After this preliminary refining the so-called *light oils* are again fractionated to obtain benzene, toluene, and xylene in a state of sufficient purity. Owing to the difficulty of purifying xylene, the latter is frequently mixed with other members of the same fraction and sold as "solvent naphtha," for dissolving resins, caoutchouc, &c.

The crude *light oil* is redistilled, and the fractions are collected according to their specific gravity instead of their boiling-point, light benzene being collected up to 0·89, heavy benzene up to 0·95, and afterwards phenol oil with a specific gravity of about 1. A residue containing naphthalene remains in the still, and distillation is stopped as soon as a sample taken in a test-glass solidifies on being cooled to 16° C. The residue in the retort is then added to the medium oil. The *light benzene* is treated with caustic soda and thoroughly well stirred, or air is driven in, in order to remove the phenols. After the separation of the light oil from the caustic soda it is treated with sulphuric acid, and finally washed. It represents crude benzene, which is distilled in a column still. The somewhat complicated treatment, with repeated washing of the various fractions, enables the pure benzene to be separated from the various commercial brands, I. to IV., and from toluene, xylene, and cumene.

Heavy benzene is washed in the same way as light benzene, treated with acid and alkali, and fractionated in the still.

The sulphuric acid from the benzene washing process contains *pyridine bases*, and is therefore called pyridine sulphuric acid. By a somewhat complicated treatment, these bases are precipitated from the acid and other impurities, and are used for denaturing alcohol or purifying anthracene.

Medium oil forms the principal raw material for the recovery of *naphthalene, phenols*, and homologous derivatives. The oil is first redistilled, the lighter fractions being added to the medium oil, the higher fractions to the heavy oil. The medium oil is then crystallised in large boxes in a separate special building. As a rule no artificial cooling is employed, and the duration of the crystallisation depends, therefore, on the temperature of the air. The masses of loose crystals deposited consist of naphthalene. The residual oil is worked up to phenols and cresols by fractional distillation, the higher fractions being treated with caustic soda. Phenol and cresol are precipitated from the waste liquors by treating them with mineral acid (generally sulphuric acid) or carbonic acid. The crude phenol and cresol obtained in this way are purified by distillation and crystallisation.

Heavy oil is at the ordinary temperature a viscous fluid mass containing a quantity of crystals in suspension. These crystalline substances are chiefly naphthalene, besides acenaphthene and certain other bodies. Naphthalene is separated from the oil by pressing, &c., and added to the naphthalene obtained from the medium oil. The residual oil chiefly contains phenols, and is mostly manufactured into disinfectants.

Naphthalene is purified by the aid of hydraulic presses or similar machines, the last traces of oil being removed by warm pressing. This naphthalene has already a rather high melting-point, but always contains impurities, which can be removed by washing the melted naphthalene with sulphuric acid at 100° C., neutralising it with caustic soda and pure water, and finally by redistillation. The naphthalene obtained from the retort may either be collected as a liquor in special moulds, where it sets into cakes on cooling, or the naphthalene vapours are led into large chambers, where they deposit as a sublimate.

More than 10,000 tons of naphthalene are produced in Germany yearly. The product is used in colour-manufacturing as a raw material for azo colours and for phthalic acid, the raw material for the naphthalene colouring matters.

Anthracene is obtained from *anthracene oil*, as a greasy, green mass, and is freed from most of the adhering oil by pressing. The pressed mass contains about 10 to 12 per cent. of anthracene, and is again treated in hot presses, a product of up to 30 per cent. of anthracene being obtained. In another method anthracene oil is allowed to cool, or is artificially cooled, whereupon anthracene crystallises out, and is forced, along with the liquid, through filter presses, which retain the anthracene. Centrifugal separators or other suitable machines are also used, and even the old-fashioned filter bags are still found in some works. The resulting mass represents crude commercial anthracene, and contains 30 to 40 per cent. of pure anthracene. The anthracene oil is generally redistilled, to recover as much of the anthracene as possible.

The crude 40 per cent. anthracene is often used direct in colour works, after being purified, or is first purified and concentrated by the tar distiller.

At the same time anthracene is separated as completely as possible from the carbazol and phenanthrene, present in considerable quantities. For this purpose the 40 per cent. pressed material is dissolved by the pyridine bases obtained from distillation. These liquid bases are able to dissolve those two substances in great quantities, whereas anthracene is only sparingly soluble. This treatment furnishes 80 per cent. anthracene, which settles down in the apparatus as a crystalline pap. It is afterwards put into a heated drying apparatus, where the final traces of adherent pyridine are removed. Anthracene obtained in this way is a soft distinctly crystalline, green powder.

Very few of the above-mentioned tar products are directly used for colour-making, and most of them must be converted by chemical processes into derivatives, suitable for reactions employed for producing the colouring matters. These products are generally called *intermediate products*, and they are partly prepared in tar distilleries and partly in colour works.

Many tar products are also utilised in other ways. Benzene and homologous derivatives, for instance, are used as solvents in many industries. Inferior coal gas is sometimes carburetted with benzene, which enriches it with carbon and improves the illuminating power. Phenol (carbolic acid) is a widely used disinfectant. Phenol also furnishes *salicylic acid*, a disinfectant and medicament that is also used in colour-manufacturing. Phenol is a source of picric acid, which, apart from its tinctorial properties, serves as a component of explosives (melinite, lyddite).

The cresols are better disinfectants than the phenols, and are used in making suitable derivatives (creoline, solutol, lysol, &c.). Naphthalene serves as a carburetting medium (albo-carbon light), as a moth destroyer, and for making lampblack. The pyridine is used for denaturing alcohol, and also as a solvent.

b. The Intermediate Products

The manufacture of these products is partly based on very complicated and difficult chemical processes, which can only be understood by those possessing a thorough knowledge of chemical reactions. Although for this reason this part of the colour-manufacturing process does not really come within the scope of the present work, it may be briefly sketched, in order to convey some idea of the way the raw materials obtained from tar are converted into the finished products, namely, dye-stuffs. It may also be mentioned that these reactions are applied not only to the raw materials, but also to effect the decomposition of the colouring matters and convert them into other colouring principles.

The most important operations in the manufacture of the chief intermediate products of the coal-tar colour process are *nitration*, *sulphonation*, and *amidation*.

Nitration is usually effected by treating the raw material with a mixture of strong sulphuric acid and nitric acid, potassium or sodium nitrate being sometimes added to the sulphuric acid. The effect of this nitrating process is that one or more of the nitro groups—*i.e.*, of the nitric acid radicle NO_2—displace hydrogen in the substance under treatment, water being formed; *e.g.*:

$$C_6H_6 + HNO_3 = C_6H_5 - NO_2 + H_2O.$$

The sulphuric acid eliminates water, and does not enter into the new compound. The details of this process vary considerably, according to the ease or difficulty with which materials can be nitrated. In certain cases it is quite sufficient to use nitric acid without any addition of sulphuric acid. The proper temperature is a matter of importance. Sometimes the ordinary temperature will suffice, at others heating is necessary, and finally in many instances the temperature must be reduced to freezing-point. The chemical nature of the materials to be nitrated and the position of the hydroxyl groups to be displaced by the nitration process also play an important part.

When several nitro groups have to be introduced into a chemical compound it is sometimes more advisable to treat the substance with sulphuric acid first, and then act on the sulpho acid with strong nitric acid, the NO_2 group in such case replacing HSO_3 groups.

Sulphonation is based on the displacing of a hydrogen atom by the group HSO_3. Sulphuric acid, H_2SO_4, is decomposed to the group $HSO_3 + HO$. The latter combines with the displaced hydrogen atom and forms H_2O = water. The details of this process also vary considerably. The sulphuric acid may be used in a dilute, strong, or fuming condition. The temperature is of the highest importance to the rapidity of the action and the position of the sulpho group in the newly-formed compound. By repeated sulphonation several atoms of hydrogen can be replaced by the sulpho group.

The sulpho acid can be converted into the hydroxyl compound by treatment with caustic soda, this reaction being employed to introduce a hydroxyl group into an organic compound. The chemical process can be explained by the following equations:

$$\underbrace{C_6H_5 - H}_{\text{Benzene}} + \underbrace{H_2SO_4}_{\text{Sulphuric acid}} = \underbrace{C_6H_5 - HSO_3}_{\text{Benzene sulphonic acid}} + \underbrace{H_2O}_{\text{Water.}}$$

$$C_6H_5 - HSO_3 + 2NaOH = \underbrace{C_6H_5 - OH}_{\text{Phenol}} + Na_2SO_3 + H_2O.$$

Phenol has an acid character. When dissolved in caustic soda or potash it gives sodium or potassium phenylate, $C_6H_5 - ONa$. Lead phenylate and other compounds are obtained in the same way. When phenol is treated with zinc dust at a high temperature benzene is formed again by reduction

$$C_6H_5 - OH + Zn = C_6H_6 + ZnO.$$

The reduction of nitro derivatives furnishes *amido compounds* by the action of nascent hydrogen. The NO_2 group is decomposed, the oxygen combining with hydrogen to form water, and the place of the oxygen is taken by two atoms of hydrogen, which combine with the nitrogen to form the amido group NH_2; *e.g.*:

$$\underbrace{C_6H_5 - NO_2}_{\text{Nitrobenzene}} + 6H = \underbrace{C_6H_5 - NH_2}_{\text{Amidobenzene (= aniline)}} + 2H_2O.$$

The chief reducing agents used are very finely divided iron (iron filings), zinc or tin, and hydrochloric or acetic acid. Hydrogen is liberated, through the formation of a metallic salt, and acts as a reducing agent.

The resulting derivatives vary according as the reduction has been effected in an acid, neutral, or alkaline solution. Electrolytic methods of reducing the nitro derivatives to amido derivatives have also been successfully used.

Direct *amidation* is effected by treating the hydroxylised combination with ammonia. This process is not always an easy one, and therefore it is sometimes necessary to use more complicated ammonium compounds—for instance, ammonium sulphite. Other operations still practically applied to obtain derivatives of the tar products and other derivatives from these include:

Fusing with caustic soda or potash, or with a mixture of these, as already mentioned.

Boiling with water, whereby amido derivatives are converted into hydroxyl compounds, the NH_2 group being replaced by OH. Ammonia is eliminated by boiling at ordinary or high pressures, also by the aid of acids (especially by sulphurous acid) or alkalies, or by diazotisation.

Chlorine, bromine, and iodine can be introduced into the derivatives, either to remain or be replaced in turn by other groups.

Oxidation is effected by means of permanganates, persulphates, and the electric current, as well as by manganese dioxide and potassium bichromate, and finally by chlorine.

These brief observations on the manufacture and treatment of intermediate products obtained from the pure chemical substances isolated from coal tar will be sufficient here. The most important of these intermediate products are therefore nitro derivatives, sulpho acids, amines, phenols, and other benzene and naphthalene derivatives. Some of these products exist as such in the tar, but most of them have to be obtained by chemical processes from simpler combinations.

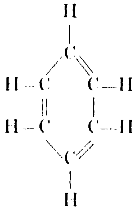
c. The Colouring Matters

Chemical Constitution, and its Relation to Tinctorial Power; Classification

The tar colouring matters are sold in the state of powder or crystals, rarely as a watery paste. In this latter case they are not soluble in water, though as a rule they are readily soluble in hot water. The shade of the powders or the crystals often differs considerably from that of their solution.

The causes of the colour and dyeing properties of these compounds have long formed the subject of investigation. Attention was naturally first devoted to the question of chemical constitution, but although the theories advanced in this connection throw a good deal of light on the chemical side of the problem, their physical properties—*i.e.*, the relations between the colour of an organic derivative and its constitution—have not yet been clearly explained. The existence of such relations is, however, beyond doubt.

All the colouring matters belong to the so called aromatic series of organic substances, and in all cases their constitution can be correlated with the typical member of this series, benzene, C_6H_6. According to the generally accepted theory, benzene, the tetravalent carbon of which is combined with the monovalent hydrogen, is constituted in the form of a closed chain, the last member of which is attached to the first one, so that a ring is formed. In accordance with *Kekulé's* theory, this ring is termed the benzene ring, or benzene nucleus, and regarded as of the following constitution:



Each atom of carbon is bound to one atom of hydrogen, and double bonds exist between some of the carbon atoms. By means of chemical reactions the single atoms of hydrogen can be replaced by other atoms or groups of atoms; the double bonds can be converted into single ones and some other monovalent atom combined on to each atom of carbon. Further substitutions can be effected in the atomic groups which have been substituted for the hydrogen atoms, and so on. Substitution of the original hydrogen atoms can be effected in one, several, or all these atoms, and several benzene rings can be linked together—in short, there is no limit to the number of derivatives from benzene.

Most of these organic bodies are colourless, but many of the derivatives differing little, if at all, from them in percentage composition exhibit a bright and peculiar coloration. Since the chemical composition does not seem to be the cause of the colour, the reason must be sought in the manner in which atoms are grouped in the compounds—*i.e.*, their structure or constitution.

Some colouring matters have been prepared synthetically, and for this reason it has been possible to investigate the question of coloration. It has also been proved that certain groups of chemical compounds possess the characteristic property of colour, and, moreover, that these combinations contain certain distinct groups of elements, the presence of which is inseparably connected with the appearance of colour.

The study of these groups of elements has shown them to be unsaturated compounds, possessing in common the property of combining with hydrogen, and thereby losing their colouring power. This is proved by the fact that all colouring matters, and especially all coloured carbon compounds, are decolorised by nascent hydrogen. These derivatives, formed from colouring matters by entrance of hydrogen, are called *leuco bodies*. They mostly contain two atoms of hydrogen more than the original colouring matter, and are reconverted into the latter by oxidation.

O. N. Witt in 1876 collected the results obtained by himself and others, and advanced a theory on the nature of the colouring matters, which may be briefly stated as follows:

The nature of a colouring matter depends on certain definite atomic groups, which give the colouring power, and are therefore called *chromophores.* Such groups are, for instance, the azo group, $-N=N-$; the carboxyl group, $-CO-$; the azine group, $=N-N=$; and also the groups $C=O$, $C=S$, $C=N-$.

When such a chromophore is introduced into an aromatic compound a coloured body is produced, which is called a *chromogen;* for instance, $C_6H_5-N=N-C_6H_5$. This body is not yet a colouring matter, but acquires that property if an acid or alkaline character is imparted by a further introduction of atomic groups—viz., when it becomes capable of forming salts. The chief of these groups are the hydroxyl group, OH, the amido group, NH_2, and others. They are called *auxochrome* groups.

The formation of a colouring matter therefore requires the presence of an unsaturated aromatic derivative an aromatic radicle, as it is called—which combines with a chromophore group to produce a chromogen. One or more auxochrome groups must enter into this combination, the presence of a carboxyl or sulpho group being of special importance.

The systematic classification of the coal-tar colours and the organic colouring matters generally is attended with great difficulties, though these are being constantly lessened by advances made in our knowledge of the chemical nature of these colouring-matters, so that those of unknown constitution form a continually diminishing class. We have already gone briefly into the classification of colouring matters according to their tinctorial properties, and will now deal concisely with that based on their chemical constitution, taking as a basis the contained chromophores and chromogens, and not the original hydrocarbons, from which the colouring matters have been derived.

1. Nitro Derivatives

These contain one or more nitro groups, and have the special property of detonating on ignition.

Their number is very large, and they are all acid colouring matters. Typical representatives of the group are, first of all, *trinitrophenol = picric acid*, $C_6H_2(NO_2)_3OH$, formed by treating phenol and other organic bodies—*e.g.*, indigo, aloe—with nitric acid. In the pure state picric acid forms pale yellow plates, readily soluble in alcohol, ether, and benzene, sparingly so in water. It dyes wool and silk a yellow shade, which, however, is not very fast. Picric acid is also used as an explosive (melinite, lyddite). *Martius yellow*, the sodium salt of *dinitronaphthol,* $C_{10}H_5ONa(NO_2)_2$, forms pale needles, and is usually sold as a sodium salt, more rarely as a calcium compound. It dyes wool and silk a golden yellow tint, and also serves for colouring spirit varnishes and food-stuffs (vermicelli), though not properly adapted to this purpose, owing to its poisonous properties. *Naphthol yellow S* is the potassium salt of dinitronaphthol sulphonic acid, and gives very fast yellow shades.

When phenols are treated with nitrous acid *nitrosophenols* are obtained, which also yield colouring matters that form very fast lakes (solid green, naphthol green, &c.).

2. Azo Colouring Matters

These form a very large class, quite different from the other groups of colouring matters, and contain as a characteristic component the chromophorous azo group $-N=N-$. This group may be present singly (monoazo derivatives) or in multiples (polyazo derivatives), and always links two benzene groups or other aromatic hydrocarbons together. Azo colours are easily obtained from phenols (azoxy colours) or amines (amidoazo colours) by the action of chlorides of diazo derivatives. They are soluble in water only when they contain a sulpho or carboxyl group. The shades obtained with these colouring matters are as divergent as their number. The more simple derivatives are yellow, a further introduction of groups into the molecule giving reds, blues, browns, and blacks; greens, however, are very seldom obtained. In the same way they are used for very divergent purposes, and will dye both animal and vegetable fibres, leather, wood, paper, straw, &c. From the chemical standpoint they are classified into: *basic azo colours* (aniline yellow, chrysoidin, vesuvine, Bismarck brown, the Höchst Janus colours, &c.); *mono-acid azo colours* (fast yellow, orange, tropeoline, metanil yellow, citronine, Indian yellow, methyl orange, azoflavine, &c.). To this class also belong the scarlet, fast red, Bordeaux red, azo magenta, &c., obtained in other ways. *Adjective azo colours* consist of non-sulphonated compounds insoluble in water, and therefore having to be developed on the materials to be coloured. One of the most important members of this class is nitraniline red, which is sold not as a finished colouring matter, but in the form of its two components, nitraniline and beta-naphthol. For use, the nitraniline is first treated ("diazotised") with sodium nitrite to azophor red, and afterwards coupled—a process that will be explained later on. Nitrosamine red must also be mentioned. The *yellow adjective azo colours* include anthracene yellow, alizarine yellow, flavazol, and diamond yellow. *Tetrazo colours* (diazo colours) are acid colouring matters giving red to black shades—Biebrich scarlet, crocein scarlet, cotton scarlet, naphthol black, brilliant black, naphthylamine black, jet black, sulphon black, and wool black.

3. Hydrazone and Pyrazolone Colouring Matters

These are very similar to the azo colours, but the sole important representative is tartrazine.

4. Azomethine and Stilbene Colouring Matters

are of only theoretical interest.

5. Oxiquinones and Quinoneoxymes

This class is of the highest importance, the colours producing, with metal oxides, bright-shaded, very suitable lakes. Alizarine, the occurrence of which in the madder root has already been mentioned, is an important representative of this class. There are various methods for preparing alizarine synthetically, but the one most used in practice is by melting anthraquinone sulphonic acid together with caustic potash. Alizarine is sold as a paste containing 20 per cent. of dry matter, and, as already mentioned, has almost entirely displaced the product formerly obtained from madder root. Alizarine dyes are very fast to soap, bleaching powder, light, and air. The shades are principally red, but blues, greens, and browns are also known. The alizarine derivatives include purpurine, flavopurpurine, and alizarine Bordeaux. Naphthol green is also an important colouring matter.

6. Diphenyl and Triphenyl Methane Colouring Matters

These colours are likewise very important, and have played a great part in the development of the coal-tar colour industry. Representative colours of this class are auramine, malachite green, acid green S, patent blue, and methyl violet, the chief, however, being the salt of the rosaniline base, fuchsin or magenta, the coal-tar colouring matter which gave the most important impulse to the establishment of the coal-tar colour industry. Aniline blue, aldehyde green, malachite green, acid green S, aurine, rosolic acid, phenolphthalein, fluorescein, eosine, rhodamine, galleine, and cœruleine are the best-known types of this class.

7. Quinonimide Colouring Matters

Toluylene blue, methylene blue, methylene green, naphthol blue, safranine, mauvein (or Perkin's violet), the first tar colouring matter made, induline.

8. Quinoline and Acridine Colouring Matters

Cyanine, quinoline yellow, quinoline red, flaveosine.

9. Thiazol Colouring Matters

Thioflavine.

10. Oxyketones, Xanthones, Flavones, Cumarines, Indones

Many of the vegetable colouring matters already mentioned belong to this class; for instance, maclurin, euxanthone, fisetin, quercitin, luteolin, morin, rhamnetin, hæmatein, brasilin, carminic acid.

11. Aniline Black

This colouring matter occupies a special position, being always produced direct on the material to be dyed, and is made by dyers themselves. It is obtained when aniline is oxidised with potassium or sodium chlorate in presence of copper, or vanadium salts under certain conditions, or by the aid of potassium bichromate or potassium ferricyanide. Aniline black is of the greatest importance, on account of the great fastness of its dyes.

12. Indigo

has already been fully dealt with. The manufacture of synthetic indigo comprises the following stages: Naphthalene is oxidised with sulphuric acid and mercury to phthalic anhydride, this latter being then treated with ammonia, whereby phthalimide is formed. This derivative is converted into anthranilic acid by the aid of potassium hypochlorite. Anthranilic acid and monochloracetic acid form phenylglycocoll-orthocarbamic acid, which yields indoxyl, and this latter is converted into indigo by oxidation with alkalis. The number of methods has recently been increased, so that nearly every colour manufacturer is now making indigo by his own special process.

The chemical constitution and other properties of the foregoing colouring matters are well known. They can therefore be systematised, which is not the case with those given below.

First comes the important class of the *sulfine colours*, already mentioned.* Next are the following:

Canarine is obtained by acting with potassium chlorate and hydrochloric acid on potassium thiocyanate, and is a sulfine colour, probably of the formula $C_3N_3S_3H$. It is a yellow powder, soluble in alkalies and alkali carbonates. It dyes cotton a light to dark yellow shade direct without mordanting, and is very permanent, except in fastness to light, which is only moderate. It is of only small importance, like *murexide*, the acid ammonium salt of purpuric acid, which is unknown in the free state. It is obtained by boiling down uric acid with nitric acid, and treating the residue (a mixture of alloxan and alloxantin) with ammonia. Murexide forms prisms with a green fluorescence, which are red by transmitted light. It dissolves in water to a bright purple-red solution, which turns violet on the addition of an alkali and is decolorised by acids. Murexide (formula, $C_8H_4N_5O_6NH_4$) is one of the oldest known artificial colouring matters, its formation having been observed by *Scheele* in the eighteenth century. In 1853 *Rumney* produced murexide on a considerable scale from guano, and up to the middle of the last century, or even later, it was largely used for dyeing and printing cottons. *Archil* and *litmus* may also be mentioned.

Whereas the foregoing classification of the coal-tar colouring matters is based on theoretical considerations, they may also be classified with regard to their dyeing properties in the following manner:

a. Basic colouring matters.

b. Acid colouring matters.

c. Adjective (mordants) colouring matters.

d. Development colouring matters, including indigo, certain azo colours, the sulfine colouring matters, &c.

Owing to the exceedingly important position occupied by organic colouring matters in consequence of the immense growth of the coal-tar colour industry, it seemed advisable to sketch briefly the systematic classification of the material, even though a full discussion of the chemistry and constitution of these colours, on which such classification is based, has to be excluded as beyond the scope of the present work.

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* By substituting sulphur for the nitrogen of the artificial indigo, the two most important representatives of this class, thioindigo red and thioindigo scarlet (see p. 467) were found in 1907, so that now all shades are known. [TRANSLATOR.]

The object of the foregoing introductory theoretical section was to inform the reader generally as to the origin, formation, and properties of the material which has to be worked, and to explain the necessity for the different methods of precipitating the various lakes. Certain technical and scientific terms current in practice had also to be explained to readers of no scientific knowledge.

Those who desire to pursue this branch of the subject further are referred to the following works : *

Die Chemie der natürlichen Farbstoffe, by Dr. Hans Rupe (Braunschweig, Vieweg u. Sohn).

Die Chemie des Steinkohlenteers, by Prof. Dr. Gustav Schulz (Braunschweig, Vieweg u. Sohn).

Chemie der organischen Farbstoffe, by Prof. Dr. Rud. Nietzki (Berlin, Springer).

Die Anilinfarben und ihre Fabrikation, by Dr. K. Heumann, continued by Dr. Paul Friedländer (Vieweg u. Sohn).

In consequence of the method of manufacture, the resulting coal-tar colours do not always possess exactly the same colouring power and intensity, but in order to turn out uniform commercial products the manufacturers standardise them to a given type by the addition of other substances. The amount of these additions is determined by a trial dyeing, and the colouring matter is standardised accordingly, so that every batch of a given brand will give exactly the same results in practical dyeing when used under standard conditions.

The substances used must necessarily be such as do not affect either the appearance or action of the colouring matters in any way, but remain perfectly inert in all the operations practised. They comprise the following: dextrin, tannin, and, especially, Glauber salt and common salt.

The commercial brands do not always represent a single colouring matter mixed together with the standardising adjuncts, but are in many cases definite mixtures of two or more colouring matters, possessing (of course) nearly the same chemical character. This is especially the case when brands are produced to match a buyer's sample, or where it is desired to improve a fast and suitable, but rather dull, colouring matter with a brighter one.

Since these colour mixtures cannot, as a rule, be detected by the eye, they are tested by blowing some of the fine dust on to a wet filter paper, whereupon the different grains in the mixture stain the wet filter paper accordingly in different shades, whilst a single colour produces merely a uniform stain.

Having now dealt with the raw materials and the manufacture of the fundamental products used in making lake pigments, we will pass to the actual preparation of the lakes. It has already been mentioned that a lake pigment consists of a carrier (the base), the colouring matter, and a precipitating agent, if this latter is really going into the lake, and does not only act as a help—*i.e.*, without being a true part of the lake. The selection of a suitable carrier (base) being of great importance, this matter will be treated under a special heading.

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* By English readers the well-known standard work *The Dyeing and Bleaching of Textiles*, by Prof. Hummel (Cassell), may be consulted for coal-tar colours and their principal applications. [TRANSLATOR.]

Carriers for Lake Pigments

In view of the diversified application of lake colours, the choice of the suitable bodies to form the base (or carrier) of the lake is often more important than that of the colouring matter—considered merely as a colouring principle—since one and the same lake will not always be equally suitable for two or more purposes. Generally a different composition of the lake is required in each case, the difference consisting in the use of a carrier suitable for the purpose in view, the colouring matter and method of precipitation, however, remaining the same. Hence, from one and the same colouring matter it is possible to get various lakes suitable for entirely different purposes, according to the choice of the carrier.

Though the properties of a practically suitable lake pigment have already been explained, the subject may be reopened, to facilitate comprehension of the substances dealt with under the subsequent headings, the more so because these lakes, which are now often used in the place of certain mineral colours, are sometimes of highly complex composition, each single component fulfilling a definite purpose.

Lakes made up with varnish, size, and oil or spirit varnish *for painting* on wood, metal, or plaster (of which there are now a very considerable number), must possess all the properties of the mineral colours, formerly used exclusively—viz., covering power, easy working, fastness to weather, lime, acids, and light. This, of course, is only possible when each of the bodies chosen for the manufacture of such a pigment possesses one or more of the above properties, so that the totality of these properties in the resulting lake will then be sufficient for all requirements. In general the carrier must possess good covering power, be easy to distribute, and able to resist outside influences, alkalies, acids, &c., whilst the colouring principle—the coal-tar colour—must be fast to light, weather, alcohol, acids, and alkalies, according to the intended purpose of the lake.

Since only a few mineral colours, except the black pigments, possess all these properties at once, and therefore the more sensitive cannot be expected to exhibit them to the same degree, the chief aim, therefore, in making these lakes is to ensure their possessing one or more of these desirable properties; and, as a matter of fact, a considerable number of lakes perfectly fast to light are known, whilst others are fast to alkalies, and still others can be worked with spirit or oil varnishes just as well as the mineral colours, whether they are used for artist's colours, fine printing, or as ordinary paints. As already mentioned, the nature of the carrier is usually of decisive influence.

The bodies mostly used as carriers are: *Alumina, artificial barytes, lead sulphate, zinc white, lithopone,* finely powdered *barytes, gypsum, whiting, china clay, starch, precipitated chalk, barium carbonate, magnesium carbonate, calcium phosphate,* the native *clays, ochre, umber, green earth, red lead,* &c.—in fact, all those insoluble bodies which can be easily reduced to a finely divided state, and the natural colour of which does not injure the desired shade of the lake.

For lakes of good covering power to be used for *ordinary painting* (with varnish, oil or spirit varnish) the carriers must, of course, have suitable properties for this purpose, like lead sulphate, zinc white, lithopone, barytes, red lead. For spirit varnish colours artificial barytes will also do.

For *wall paper lakes*, which are generally required cheap, use is made chiefly of *alumina, artificial barytes, barytes, whiting, clay, starch, ochre, umber,* and ordinary *white* and *coloured clays*, more seldom *green earth.*

Lakes used by makers of *fancy papers* must be very finely divided, of good covering power, and furnish a uniform coating when applied. Hence for this purpose *alumina, artificial barytes, china clay, precipitated chalk, barium carbonate* and *magnesium carbonate, clay, ochre, umber*, and less often *whiting*, are used.

Lakes for *printing inks* and *artist's colours*, the finest and most valuable of all, contain, when made as transparent pigments, *alumina*, either alone or mixed with *artificial barytes*, whilst if desired to be more or less opaque pigments they will also contain *lead sulphate, zinc white*, or *lithopone*, and in some cases *red lead.*

Lime colours contain only *green earth, white* or *coloured clay, ochre, barytes,* or *gypsum* as a carrier, the two latter, however, being always mixed with one or more of the others, the latter therefore forming the principal part of the carrier.

Alumina (*Aluminium Hydroxide*, $Al_2(OH)_6$)

Aluminium hydroxide is the most important carrier, and is nearly always present in the best lakes. It is used as such, or produced at the same time as the colouring matter is precipitated. In a nearly pure state, or at the most mixed with a little artificial barytes—which is generally precipitated at the same time—it serves as carrier for most printing inks, and then forms the principal part of the base.

On the other hand, good lakes for wall and fancy papers contain more artificial barytes than alumina, and therefore both bodies are precipitated at the same time as the colouring matter. An addition of artificial barytes must generally be given, or else the quantity of sodium sulphate formed when alumina is produced must be increased by a certain addition of crystallised or calcined Glauber salt.

The nature of, and suitable method of producing, the alumina used in lake-making are therefore of the greatest importance; and although good commercial alumina is quite suitable, its preparation in the works is often a matter of necessity, the former article being seldom in such a fine state of division as that obtained by direct precipitation. Moreover, in many cases the whole operation is based on the simultaneous precipitation of the colouring matter and alumina with or without artificial barytes (or other bodies).

Aluminium hydroxide, $Al_2(OH)_6$, generally called "alumina," is always produced when soluble aluminium salts are treated with caustic alkalies or alkali carbonates, the product, however, varying according to the salts used. Alumina produced by the aid of caustic alkali—caustic soda or potash—is always a slimy or gelatinous mass, whether prepared by the cold or by the hot method. When dry it is very hard and horny. It dissolves in an excess of the precipitating agent, and is therefore of no use for lake-making.

For many purposes (referred to later on) a solution of alumina in caustic soda, the so-called *sodium aluminate*, is used, and is sold in the solid form.

Alumina precipitated by alkali carbonates, however, has quite different properties; it is insoluble in excess of the precipitant, and is less mucinous, even from dilute cold solutions, than that made from caustic alkalies. When produced at a high temperature, and from not too concentrated solutions, it is opaque, pure white, and in the dried state is soft and powdery.

The raw materials for manufacturing alumina are aluminium sulphate, alum, and calcined or crystallised soda. The chemical changes occurring in the reaction are briefly as follows: The sulphuric acid of the aluminium salt combines with the sodium of the carbonate, and insoluble alumina is precipitated on addition of water, whilst carbonic acid escapes with effervescence* and Glauber salt remains in solution. The formation of the alumina proceeds gradually and by stages, basic aluminium sulphate being first formed, and then progressively deprived of its sulphuric acid by the further addition of sodium carbonate, until when boiled with an excess of the latter the loss of acid is complete. The different phases may be represented by the following equations:

$$Al_2(SO_4)_3 + Na_2CO_3 + H_2O = Al_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2$$
$$Al_2(SO_4)_2(OH)_2 + Na_2CO_3 + H_2O = Al_2SO_4(OH)_4 + Na_2SO_4 + CO_2$$
$$Al_2SO_4(OH)_4 + Na_2CO_3 + H_2O = Al_2(OH)_6 + Na_2SO_4 + CO_2$$

Practically the precipitation is effected at or very near the boiling-point. A boiling solution of alum or aluminium sulphate is treated with a hot solution of soda in a very large tank, with constant stirring, until no further escape of carbonic acid can be observed on continued boiling and addition of soda solution. The liquor in the tank will then have a slightly alkaline reaction.

The product must be washed to recover the perfectly pure alumina, but as the sodium sulphate is very obstinately retained by the alumina precipitate, unless very large tanks can be used, a frequent change of water is necessary, until barium chloride produces no precipitate, or only a slight whitish mist, with the washings. Boiling and rapid stirring will greatly accelerate the troublesome washing process, especially when hot or boiling water is used.

The temperature and concentration of the solutions greatly influence the nature of the resulting aluminium hydroxide, as does also the presence, after the precipitation, of an excess of one of the two applied salts. If very hot or strong solutions be used for the precipitation the alumina is thrown down in a lumpy or granular state, owing to the too violent liberation of carbonic acid, whilst with very dilute and cold solutions it is obtained in a gelatinous, transparent state, of little covering power when dried. In this state washing is a very difficult process. The basic aluminium sulphate first formed settles very slowly, and therefore when very dilute and cold saline solutions are used a large quantity of soda must be added before the carbonic acid begins to come off and aluminium hydroxide is formed. This is a very important point in the manufacture of many lakes from basic coal-tar colours.

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* It may be mentioned as a curiosity that in a leading German colour works the carbonic acid escaping during the manufacture of a pigment colour (and generally going useless into the air) is collected, purified, and sold. [TRANSLATOR.]

Except when the colouring materials are very sensitive to alkalies, an excess of soda in the precipitating process is usually no disadvantage unless for reasons of economy. An excess of aluminium sulphate, however, causes the formation of crystalline double compounds of the hydroxide with the excess of sulphate, and renders the precipitate granular, rough, and unsuitable, especially for lakes in paste form. In view of these circumstances, it is desirable to adjust the proportions of the saline matters so that after the precipitation neither aluminium sulphate nor soda is present in excess.

To obtain a pure white alumina, free from other combinations, it is of course important that pure raw materials should be used — viz., the best commercial qualities: perfectly dry powdered, pure white aluminium sulphate, with the largest possible content of aluminium oxide, Al_2O_3 (the maximum being about 16 per cent.). Poorer brands of sulphate, especially those sold in lumps contain only 11 to 15 per cent. of oxide, owing to the higher content of moisture. Though the presence of iron in the aluminium sulphate is not so prejudicial for most lake pigments as is generally believed, only brands with a minimum of iron should be used.

Aluminium sulphate perfectly free from iron is seldom obtainable at a reasonable price, but that containing ½ per cent. of iron is easily procurable, and is suitable even for manufacturing the alizarine and azarine lakes, which are very sensitive to iron salts. For making alumina absolutely free from iron, alum is preferable, the commercial salt being practically free from iron, though, of course, it is dearer than aluminium sulphate. Alum is also more suitable for making finer azo colour lakes for printing purposes, for which a higher price can be obtained, the precipitates obtained from alum and barium chloride generally giving softer and brighter tints and lakes of better covering power and intensity than the corresponding aluminium sulphate lakes.

Ammonia soda is the most suitable commercial salt, though crystal soda is used in some cases. Of course, the purest kinds must be chosen, and the crystals must be quite free from Glauber salt.

It is only in very few cases that alumina is used alone as a carrier for lake pigments; more frequently it is precipitated in well-defined quantities directly upon other bodies, like *artificial barytes, barytes, lead sulphate, china clay, red lead*, &c. The process is the same in all cases. The carrier, mixed with water, is passed through a sieve into a precipitating tank, the hot solution of aluminium sulphate is run in, and finally the solution of soda is slowly added, with continual stirring. By this simple method a most intimate mixture of the hydroxide and the other bodies forming the carrier is obtained, the dissolved aluminium sulphate penetrating, so to speak, the individual particles of these bodies, and these are covered by the deposited alumina the more completely in proportion to the degree of dilution maintained. If lakes made from bodies so mixed are to be used in the dry state and alumina is not predominant in the mixture, its physical character has usually little influence on that of the dry lake. In such case the hydroxide can be precipitated with strong or dilute, cold or hot saline solutions, unless the shade of the lake is likely to suffer. The carrier made from such mixtures is washed in the ordinary way, and, on account of the high specific gravity of the materials, is effected more rapidly than with alumina alone.

A great many carriers, however, are not washed before being coloured, the Glauber salt being converted into artificial barytes by an addition of barium chloride, and utilised as a further component of the carrier. This method is the more practical since it gives a better fixation of the acid coal-tar colours, most of which are completely precipitated by barium chloride.

A special method, suitable for many acid coal-tar colours, consists in decomposing aluminium sulphate with milk of lime or levigated chalk. Besides aluminium hydroxide, this treatment produces a very light and voluminous form of gypsum, which is partly reconverted into artificial barytes when the colouring matter is afterwards precipitated with barium chloride. Lakes obtained in this way are said to be specially soft, and often specifically lighter than usual.

For certain lakes lead sulphate is prepared in the same way, lead acetate or nitrate being used as the precipitating agent instead of barium chloride. When the coal-tar colour—for instance, eosine, erythrosine, phloxine, rose Bengale—can be precipitated by these salts, it is fixed at the same time as the lead sulphate, in the same way as mentioned in the case of barytes. In some cases, and especially when these lead salts are not employed as lake-formers, the lead sulphate is added direct to the alumina, for the sole purpose of increasing the covering power.

A more difficult process, on account of liability to alteration, is the precipitation with arsenic, phosphorus, stannic acid, or resin, combined with the precipitation of alumina, in which the corresponding alumina salts are formed in addition to aluminium hydroxide, and act as direct, slightly acid lake-formers.

Arsenious Acid, H_3AsO_3, obtained by dissolving arsenic trioxide, As_2O_3 (ordinary arsenic), in water, is too easily decomposed to be suitable for lake-making, and therefore the more stable sodium salt obtained by dissolving arsenic in a solution of soda is used. The concentration of the soda solution and the duration of boiling play a considerable part. As a rule the solution of arsenic gives the better results in proportion to its degree of dilution and the longer it is boiled; but it is useless to boil longer than one hour, and thirty to forty minutes will generally be sufficient. The resulting solution of arsenic is, with few exceptions, added slowly and with continual stirring to a hot solution of aluminium sulphate, containing the colouring matter in solution. The reverse procedure is adopted with certain basic colouring matters, the solution of arsenic, cooled to about 50° C., eventually diluted with cold water, being precipitated by the hot solution of alumina, and the solution of the colouring matter added afterwards. In this case the latter must be fixed by other precipitating agents, but the lake is particularly soft and smooth, settles down quickly, and is easily washed.

In both methods, however, certain precautions must be taken. The correct proportion of arsenious acid and soda is very important, an excess of arsenic injuriously influencing the physical properties of the lake even a long time after use, besides being uneconomical, and under certain circumstances prevents the absolute fixation of certain of the basic coal-tar colours, The necessary quantity of arsenic depends, therefore, on the capacity of the arsenious acid to form a lake with the colouring matter in question, and differs with each group of the basic colouring matters.

Of no less importance in the precipitation with arsenic is the alkaline or acid character of the solutions. If the precipitation is effected in a strongly acid solution, the precipitate is mostly very fine, settles down slowly, and cannot be easily washed, on account of its gelatinous and sludgy condition, whilst the finished lake very obstinately retains the adhering water, is difficult to press, dries badly, and darkens in colour on drying, thus losing its warmth and brilliance of tone. From alkaline solutions the lake comes down in a more voluminous and softer condition, but the free alkali either destroys most of the basic coal-tar colours in a very short time or prevents suitable fixation—sometimes in a very disagreeable manner. In the most favourable case alkaline precipitation is as unreliable as the acid method, and therefore a neutral or even slightly acid character of the solution is preferred, being, moreover, not difficult to obtain by an accurate calculation of the quantity of the materials and by a careful supervision of the process.

The chief of the chemical auxiliaries added to the solutions for the purpose of regulating the decomposition—viz., to produce and maintain neutrality, or even to reduce the acid character—is alkaline sodium acetate, the effect of which is probably explicable as follows: The greater affinity of the sulphuric acid for the alkali sets up a reaction between the aluminium sulphate and sodium acetate, an excess of aluminium acetate being produced, which has less influence on the precipitation.

Precipitations based on a combination of alumina with *aluminium phosphate* as a carrier, in which the latter acts at the same time as lake-former, are generally performed by adding a solution of acid sodium phosphate, treated with soda, to a solution of aluminium sulphate, already containing the colouring matter. The addition of soda to the solution of sodium phosphate must be done in certain definite proportions, in order to obtain a perfectly neutral precipitation. From an acid solution the precipitate would fall down in a gelatinous state, whereas with an excess of alkali a quantitatively complete precipitation is impossible. Here again the concentration and temperature of the solutions are of special importance. If the liquids are too dilute or too cold, the resulting lake has very little covering power, dries exceedingly slowly, on account of obstinately retained moisture, and is liable to form afterwards a vitreous and poorly coloured mass. Precipitated from over-concentrated solutions, the dried lake is softer, but the precipitation of the colouring matter is irregular, and the dry lake streaky and spotty on the surface of fracture. Hence the precipitation is preferably effected with 10 per cent. solutions and at boiling heat, the liquors being stirred continually.

Alumina-tin compounds are now seldom used as carriers for lakes, stannous chloride—"tin salt"—and stannic chloride being the only salts employed, though stannic acid and metastannic acid are sometimes taken into consideration. As a rule lakes obtained by precipitation with tin compounds are very liable to variation, and the results of one and the same process are seldom uniform, especially with regard to intensity and shade. This uncertainty may explain why tin compounds are now shunned as precipitating agents. On account of its powerful reducing action, stannous chloride is rarely used as a direct precipitating agent, the lakes obtained being rarely bright and full, but needing correction with other agents, such as tannin. As a raw material for stannates, it gives better results, however, especially with certain green and blue basic coal-tar colours.

The effect of stannic chloride, however, is based on its decomposition, in an alkaline solution, to tin hydroxide, which, at the moment of precipitation, throws down the dissolved colouring matter as a tin lake, if the solution is not too strongly alkaline in character to produce a lake. These precipitations are of no practical value, and are now only used with certain vegetable colouring matters, especially Persian berries.

Tin combinations are generally introduced into the alumina carriers by mixing the salt with aluminium sulphate or soda, according to the nature of the colouring matter in question, the corresponding aluminium-tin compound being formed and precipitated at the same time as the alumina.

In certain cases nitro-, azo-, acid-, and resorcine colouring matters should be precipitated in presence of alumina by lead hydroxide, zinc, or the alkaline earth metals. In this process the solution of colouring matter is mixed with alumina, and the metal or hydroxide of the alkaline earth metal is added in a freshly precipitated, washed state, mixed with water. Many lakes obtained by this process are specially fast to water and alcohol.

Barytes and Artificial Barytes

Though *artificial barytes* is nearly as largely used as alumina for lake-manufacturing, pigment colours rarely contain artificial barytes alone as a carrier—in fact, only those prepared by the simultaneous precipitation of the colouring matter with barium chloride and Glauber salt, whereby the quantity and the nature of the precipitated colouring matter impart properties to the lake that facilitate the finishing of the product, viz., filtering, grinding, sifting, &c., and especially improve it for certain uses.

The method of precipitating colouring matters directly on freshly precipitated or levigated commercial artificial barytes is now seldom practised, the lakes obtained in this way being of no great value, since they are difficult to work, very heavy, and dry very quickly and hard. On account of their great covering power, they mostly form shiny coatings when used as distemper colours, and exhibit numerous defects when used in wall-paper printing or for printing inks. All these disadvantages are considerably diminished or entirely removed by adding a specifically lighter body of lower covering power to the artificial barytes. For fine colours alumina is almost exclusively used for this purpose; for medium qualities starch, china clay, ochre, &c.; and for painter's colours barytes, zinc white, lithopone, &c. In the former case, according to the nature of the colouring matter used, the alumina and artificial barytes (commercial brands) are mixed by mechanical means, or are precipitated in common, with or without the colouring matter, as described under the previous heading. With many colouring matters both methods often give the same result. As regards the other qualities of lakes, the respective bodies are incorporated mechanically before or after the precipitation of the colouring matter, the materials being mixed with water and run in through a fine sieve.

Barytes is largely used for making lakes, all such as serve as ordinary painter's colours containing barytes as a carrier, though generally in admixture with other bodies of greater covering power. Painter's colours being used for various purposes, nearly every existing brand of barytes, from the finest to the poorest, pure white, reddish, or grey, is found as an ingredient of such lakes. Good brands of wall-paper lakes, especially if sold in paste, must not contain any considerable quantity of barytes, because such lakes settle down quickly and firmly in the colour ducts of the printing machine. On account of their stiffness and low covering power, the colours are also unsuitable for grounding purposes. A thick uniform coat could be obtained by using the paint in a thick condition, but then the viscosity would come into greater prominence, and the coating would become hard, rough, and mostly very dull. Hence lakes containing barytes cannot be used for colouring fancy papers.

The other materials mentioned under the heading "Carriers for Lake Pigments" are of much less importance. Their use will therefore more suitably be discussed in the practical part which deals with the way in which each is employed.

Manufacture of Lake Pigments

The theory of the formation of lake pigments has not yet been clearly enunciated. Only in a few cases can lake pigments be regarded as chemical combinations in the true sense of the term, since there is no combination of the colouring matter, base, and precipitating agent in equivalent proportions that could be calculated for in the case of colouring matters of known composition and constitution. The precipitating agents, salts or acids, are mostly added in excess, so as to obtain complete precipitation, as well as for shading purposes. In other cases less than the calculated quantity of the precipitating medium is used, the finished lake then containing, of course, a certain amount of colouring matter in the free state, mechanically fixed by the precipitation process. One molecule of magenta, for instance, requires theoretically one molecule of tannin, but about one-third of this quantity is sufficient for complete precipitation.

As already mentioned, the lake is obtained either by fixing a colouring matter on a carrier without any precipitating agent, and in this case the process must be regarded as chemical combination or mechanical mixture—*i.e.*, an absorption; or else the colouring matter is precipitated from its solution on to the carrier by the aid of a precipitating agent and fixed. In the latter case it combines with the precipitating agent to form an insoluble combination mechanically fixed on the carrier, or forms a double compound. In point of brightness, intensity, and fastness to light and air, the lakes obtained by precipitation are generally superior to those prepared by a simple process of coloration. It is therefore questionable whether these latter pigment colours really can be regarded as lakes in the proper sense of the word.

It may be mentioned here that basic and acid colouring matters can also combine and precipitate one another. This property is sometimes used for shading purposes; but since the resulting lakes are generally not fast, this reaction can only be used with caution.

The operations and the plant used for manufacturing lakes at the works are the same as described in the manufacture of artificial mineral colours, but certain hints and rules may be given here, with reference, for instance, to *dissolving the colouring matter.* As already mentioned, the colouring matters are used dissolved in water, and it is only in a few special cases that a pure alcoholic solution is necessary, though larger or smaller quantities of alcohol, acetic acid, and other bodies are sometimes added to the water in order to obtain complete solution.

First of all the character of the water used as the solvent is, of course, very important. Many coal-tar colouring matters, being very sensitive to salts of lime, chalk, magnesium, and iron, must not be dissolved in hard water, and in such cases the condensed water from the steam pipes is best when a supply of soft water is not available. The temperature of the solution should generally not exceed 60° to 70° C., because many coal tar colours become considerably reduced in brightness or are spoiled entirely at higher temperatures, or when boiled, the lakes also suffering accordingly.

Most coal-tar colours are readily soluble in water, and therefore the prescribed quantity of hot water is simply poured over them, or they are placed in the water in small portions, with continued stirring, until completely dissolved. Should the colouring matter dissolve with difficulty in water, it is generally mixed to a thin paste with water, or by an addition of alcohol or acetic acid, the necessary quantity of water being then slowly stirred in. Wooden, copper, enamelled or galvanised iron tanks are used, provided the material of the tank has no action on the colouring matter, or does not affect its shade in any way. The coal-tar colours being sold by the aniline colour makers in a perfectly pure state, it is rarely necessary to filter their solutions.

Passing now to the practical part of lake-manufacture, it is necessary to proceed systematically, so as to facilitate understanding the suitable treatment of the complex material. For this purpose the most suitable classification of the various coal-tar colouring matters is that based on the common methods of precipitation, as follows:

1. Coal tar colours precipitated by the aid of *barium chloride*, viz., all the *acid coal-tar colours.*
2. Coal-tar colours precipitated by the aid of *lead salts* (lead acetate or nitrate); notably the *resorcine colours*—eosine, erythrosine, phloxine, rose Bengale.
3. Coal-tar colours precipitated by *tannin* or *tannin-tartar emetic.* These chiefly comprise all *basic coal-tar colours.*
4. Coal-tar colours precipitated by *aluminium oxide*, Al_2O_3: the *rosaniline*, and *alizarine colours* only.
5. Colouring matters *directly* produced by *precipitation: ice colouring matters, diazo colours.*
6. Colouring matters directly absorbed by *siliceous material* (clay, green earth, umber, ochre, &c.), viz., the *basic coal-tar colours* only.

Of course there are exceptions to the foregoing classification, inasmuch as colouring matters of one group may be precipitated by media of another group. For instance, certain of the azo colours are precipitated completely by lead salts; and, conversely, some of the basic colours will, under certain conditions, form suitable lakes with barium chloride, or at least are absorbed and retained by lead and barium chloride lakes, without any further precipitating agents—*e.g.*, magenta, rhodamine, brilliant green, methyl violet, &c. In this way *the combined or mixed lakes* are obtained, and on account of their large number they play a more important part in lake-manufacture than the pure lakes obtained from a single colouring matter by one of the above-named precipitation methods.

A full collection of all the suitable formulæ for the various lakes cannot, of course, be expected here. Only a few examples can be given to explain the method, the preparation of the solutions used, the quantity and kind of the dry adjuncts, the relative advantages, &c. The various exceptions to the different methods are quickly learned by experience. When a colouring matter of which the lake-maker has had no previous experience has to be treated, the colour-makers will always give the necessary particulars as to its use, the most favourable method of precipitation, &c. We are now solely concerned with lakes used in practice as *pigment colours*.

Whilst, as already mentioned, the covering power of the lake pigments depends chiefly on the composition of the carrier, the colour and other properties of the lake—fastness to light, alkalies, weak acids, alcohol, &c.—depend entirely, or for the most part, on the nature of the colouring principle—*i.e.*, one or more coal-tar colouring matters. It follows, therefore, that, apart from the possibility of their precipitating each other, the colouring matters chosen must supplement one another's properties, so as to enable products to be made that will satisfy all requirements. A thorough knowledge of the coal-tar colours is therefore a prime condition for the successful manufacture of lake pigments.

In view of the great number of coal-tar colours now known, the possibilities of combined precipitation are practically unlimited. In modern colour-making the precipitation is not always carried out according to the methods given above, but sometimes on lines that are really absurd, for the sole purpose of throwing imitators off the scent.

An ordinary maroon lake for wall-papers may be taken as an example of a combined lake. As the initial lake—if such a term be permissible—a scarlet lake is almost invariably chosen (see p. 432 for the process). According to the foregoing classification by methods of precipitation, this lake belongs to Class 1. When completely precipitated with barium chloride, the bright red lake is converted into the dark, bluish or brownish maroon shade by a solution of magenta, which is either fully absorbed or afterwards fixed, if in excess, by an addition of barium chloride. Since magenta belongs to the basic colouring matters, it must be precipitated on the scarlet lake by means of the tannin-tartar emetic method (Class 3). The shade and intensity of the maroon lake depend on a variety of circumstances. According as a bluish or yellowish scarlet, for instance, or a pure orange, or even all three together, has been used for the scarlet lake, the finally added magenta will produce a bluish, brownish, or dark red shade, which, if the lake is also precipitated on one or more mixed carriers, may in turn be influenced by the nature of these various components. Moreover, the shade of the maroon lake can be modified at pleasure to a bluish or brownish tone by a simultaneous precipitation of other basic coal-tar colours, such as methyl violet, brilliant green, &c., added to the solution of magenta. There being no reliable methods of detecting individual coal-tar colours, especially in a mixture of several, the matching of a mixed lake pigment is often a very difficult and troublesome task, and the sole guide is an experienced eye and skill in the analysis of colour (see Translator's remark under the heading "Analysis of Lake Pigments").

1. Lakes Precipitated by Barium Chloride

a. Yellow Lakes

For reasons very easy to understand, yellow lakes are made and used as true pigments to a smaller extent than any other lakes, owing to the superior advantages presented by the absolutely fast and very bright lead chromates of high covering power and low price. Yellow lakes, the number of which is very limited in comparison with the extensive scale of red, blue, and violet lakes, are more often found as components of pure green or olive lakes, the brightness and intensity of which are thereby considerably improved.

The acid yellow coal-tar colours, *quinolin yellow*, *naphthol yellow*, *paper*, *Victoria*, *dianil*, and *azo yellow*, and more recently *astacine yellow*, are used for manufacturing lakes. Quinolin, paper, and azo yellow are completely precipitated by barium chloride, but naphthol yellow and astacine yellow require the presence of alumina and artificial barytes as well to ensure the same result. Except in the case of quinolin yellow and (under certain conditions) paper yellow lakes, the filtrates and washings are always slightly tinged with yellow, in spite of the complete precipitation of the colouring matter—a sign that these lakes are not sufficiently fast to water.

Quinolin and azo yellow require 100 parts of water to 1 part of colouring matter, but the others only need 50 parts for complete solution—a fact fully explaining the easier precipitation of the first two named colouring matters by barium chloride and the greater fastness of their lakes to water. Naphthol and astacine yellow, however, are more difficult to precipitate under the conditions mentioned; and when a larger quantity of the colouring matter is used—viz., brighter shades are made—complete precipitation is effected only after a prolonged and continual stirring.

The imperfect fixation, however, can be supplemented by adding a small quantity of barium chloride, soda, or aluminium sulphate, either alone or together. For this purpose the filtrate of a sample taken from the manufactured lake is divided into three parts, each being tested with one of the three salts named, to see whether a precipitate is formed and if complete fixation of the colouring matters has been secured. If no satisfactory result is obtained, the test must be repeated with two of the salts—barium chloride and soda, aluminium sulphate and soda, or barium chloride and aluminium sulphate—and, if necessary, with all three together, the proportions consumed being noted and calculated for use on a practical scale. It must not, however, be expected that the first attempt in practice will be satisfactory, for, owing to some unexplained reason, this is rarely the case, and further tentative trials must be made. This peculiarity is frequently observed in the precipitation of other acid colouring matters, and not yet entirely explained. The fact was therefore mentioned in this place to avoid any further discussion of the matter.

Owing to the property of quinolin and azo yellow to form lakes direct with barium chloride, these colouring matters can be used alone or mixed together in any desired quantities for manufacturing simple or mixed lakes without any further adjuncts. For this purpose they are precipitated on some colourless body, such as barytes, china clay, ordinary clay, gypsum, zinc white, lithopone, &c., by a solution of barium chloride. Finer lakes, such as are used in paste or powder form for wall and fancy papers, generally contain artificial barytes and alumina as a carrier, barytes and china clay (more rarely chalk, gypsum, or starch) being added to reduce the cost.

The following proportions may serve as an example of the first type of lakes.

I. 100 barytes (or china clay, clay, &c.).
1 to 5 quinolin yellow (1 : 100 water).
2 to 10 barium chloride (1 : 10 water).

II. 100 barytes (or china clay, clay, &c.).
1 quinolin yellow } (1 : 100 water).
1 azo yellow }
2 to 3 barium chloride (1 : 10 water).

The precipitation on alumina and artificial barytes is usually effected as follows: Aluminium sulphate is dissolved in a forty-fold quantity of hot water, and a solution of calcined soda in ten parts of water is slowly run in, with constant stirring. A mixture of alumina and Glauber salt is produced, which is mixed by continual stirring with the colouring matter, dissolved in 100 parts of hot water (50° to 60° C.), followed by the warm solution of barium chloride (1 : 10), the whole being stirred until the colouring matter is completely fixed on the carrier, a process sometimes taking several hours. By the aid of trials made on filter paper, as already mentioned, with a few drops of the colour liquid, it is ascertained whether the lake is entirely precipitated or not. A drop of the well-stirred contents of the tank should give a coloured stain with sharp edges when dropped on the paper, the surrounding wet zone being colourless, otherwise the lake is not yet entirely precipitated and the water still contains dissolved colouring matter. The necessary quantity of barium chloride varies in each case, depending on the quantity of the colouring matter, a certain additional quantity being needed to fix the colouring matter.

Example: 20 aluminium sulphate (1 : 40).
10 calcined soda (1 : 10).
5 to 10 colouring matter (1 : 100 resp. 1 : 50).
34 to 50 barium chloride (1 : 10).

The lakes are washed as usual, but since the yellow lakes are not very fast to water the washing is not continued until all the sodium chloride has been removed, excessive washing reducing the brightness of the lakes. If the washing water runs away coloured (*i.e.*, the colour "bleeds"), a small quantity of the precipitating agent (barium chloride) is added as a substitute—though an imperfect one—for the after-precipitation. The "bleeding" of the colour is the more pronounced the smaller the proportion of salt in the washing water.

b. Orange Lakes

The above-described methods of precipitation and the quantities of raw materials are, with a few very insignificant exceptions, also employed for the manufacture of orange lakes from suitable coal-tar colours, so only the different characteristics of the types of this group need be given here.

Practically all the commercial brands of orange colouring matters can generally be used for manufacturing lakes, *orange II*, put on the market in about the same quality and strength by all aniline colour works, being, however, preferred to all others on account of its cheapness, because, if made according to directions, very bright and fairly fast lakes can be obtained. In addition, *orange R*, *orange O*, and *fast orange O* are used for certain orange lakes, purer shades especially for printing purposes being made from *brilliant orange G and R*, whilst the differently toned brands, such as *helio orange, pluto orange, mandarin orange for lakes*, &c., are only used for special purposes, that, of course, cannot be discussed here.

All these brands of orange are readily soluble in hot water (1 : 50), and are completely precipitated by barium chloride alone in nearly all cases. Most of these lakes, however, are not bright, and the precipitation is not a complete one unless it is effected at a higher temperature (60° to 70° C.). With many brands of orange coal tar colours, however, the higher temperature influences only the brightness of the lakes in a favourable way, whilst the complete fixation of the colouring matter only takes place on cooling.

Though, as already mentioned, barium chloride alone will precipitate most of the orange coal-tar colours completely by itself, this very simple method is only seldom used. Generally, even with quite ordinary brands, artificial barytes is produced at the same time, because the colouring matter is apparently not only fixed better and rendered faster to water, but the resulting lake is also purer in tone, without being affected by the presence of barium sulphate, provided the latter is not in excess. This fact becomes all the more noticeable when, as is done with the finer brands of orange lakes, alumina is also produced at the same time. In this case the precipitation of the colouring matter is so complete that the filtrate from the lake is quite colourless, a rare occurrence when the colouring matter is precipitated along with artificial barytes. Here, too, it may happen, especially when the ratio of colouring matter to barium sulphate is very high, that the fixation of the colouring matter is supplemented by an after-precipitation with one of the salts used, though the calculated quantity of barium chloride should have been sufficient for complete precipitation. This circumstance, however, occurs in but few brands of orange II, the others, especially fast orange O, orange R, brilliant orange G and R, being usually precipitated completely.

The following quantities of raw materials will serve as a typical example for ordinary orange lakes :

100 barytes (mixed with zinc white, lithopone, &c., for opaque colours).
5 Glauber salt, cryst., dissolved in 50 water.
3 to 5 colouring matter, dissolved in 50 to 100 water.
8 to 10 barium chloride, cryst , dissolved in 80 to 100 water.

Any after-precipitation, if necessary, is usually effected with 0·5 to 1·5 of Glauber salt.

In many cases the alumina soda method can be specially recommended for producing very bright lakes from orange coal-tar colours.

c. Red Lakes

Compared with the above-mentioned yellow and orange lakes, the number of red lakes is relatively much larger, and their manufacture and consumption are so great that the other lakes—viz., the blues and violets—cannot vie with them in this respect. The chief colouring principles used for manufacturing red lakes are first of all the so called *azo colours*, generally known in the colour trade as *scarlets*. They are obtainable in all varieties, from the lightest scarlet to the very darkest and most bluish Bordeaux shade. Most of these colouring matters, too, are readily soluble in water, and are completely precipitated from their solutions by barium chloride. All possible varieties of the barium chloride precipitation method are used for this purpose in colour works, the decisive factor being the physical or chemical nature of the colouring matter or the brilliance of the lake to be produced.

To simplify this complex subject it will be useful to examine first of all the various and, with regard to rent, suitable methods of precipitation with barium chloride that differ either among themselves or in the results which they give with apparently analogous colouring matters, before dealing with the separate types of colouring matters and their lakes.

The true *aluminium sulphate and barium chloride method*, in which aluminium sulphate is first precipitated by soda, and the resulting Glauber salt then thrown down along with the colouring matter by barium chloride, is the one generally used in manufacturing red lakes. This method, however, is not applicable to all the azo colours, since many of these colouring matters are very difficult to precipitate completely, or, if such is the case, sometimes form peculiar brownish lakes. This discoloration, however, is common to nearly all azo colours precipitated by this method when the solutions of the salts employed are too concentrated, too excessive dilution being the cause in other cases, whilst in others, again, discoloration occurs in the drying-room, even when the precipitated lake has been thoroughly washed. Generally speaking, all the lakes from azo colours made by this process undergo sometimes considerable changes while in the artificially heated drying-rooms, especially if the temperature is irregular or too high. Hence this cheapest method is specially confined to the manufacture of red lakes in paste form, the temperature of the precipitation then playing a very important part. Only a few of the scarlet lakes become apparently brighter if hot solutions are used for precipitation (90° C.), most of them being more or less pale or really discoloured, especially when, at the same time, the saline solutions have been too strong. Hence in all the precipitation methods for these colours very dilute solutions and a low temperature—not above 40° C.—are essential. The most suitable alumina for paste colours, however, being only obtainable at a very high temperature (boiling heat), whilst the colouring matter must be precipitated not below 40° C., the solutions of aluminium sulphate and of soda are therefore generally mixed in a heated condition; the warm solution of the colouring matter is well stirred and added, the mixture diluted with a suitable quantity of water, and finally precipitated by a *cold* solution of barium chloride. The fixation of the colouring matters usually proceeds very slowly, either in consequence of the degree of dilution or on account of their chemical nature, and the mixture must therefore be stirred for some time after the precipitation is complete.

In the *alum and barium chloride process* aluminium sulphate is replaced by an equivalent quantity of crystallised alum, though in all other respects the two processes are identical. To obtain brighter red lakes a corresponding quantity of soda crystals is said to be preferable to calcined soda, but this opinion is probably correct in only a very few instances. As a matter of fact, the lakes obtained by the alum method, especially from dilute solutions, are not only softer and sometimes brighter in tone, but also much softer, lighter, and of greater covering power when dry, so that they are especially suitable for certain printing purposes. Of course the price of alum makes these lakes considerably dearer than those from aluminium sulphate, especially when crystal soda is used as well, so that this method is not suitable for wall-paper lakes unless the colouring matter cannot be completely precipitated by the other.

The *aluminium sulphate and lime process* has latterly been growing in favour for precipitating certain red azo colours. It consists, as already mentioned on p. 484, in decomposing aluminium sulphate with caustic lime in the form of a freshly prepared, very pure milk of lime, a certain quantity of calcium sulphate being formed as well as alumina. For this reason the dried lakes made after this process are soft and light, unless the calcium sulphate be converted into artificial barytes by the barium chloride. Aluminium hydrate obtained by this method seems also to be of a different character, since the low specific gravity and the softness of these lakes cannot be entirely due to the relatively small quantity of calcium sulphate. Sometimes the azo colours require a certain addition of Turkey red oil to ensure complete fixation, a favourable influence being also exerted on the physical properties of the dry lake.

Generally the aluminium sulphate and lime process is not characterised by specially uniform results, for unless the prescribed state of dilution be exactly maintained alumina easily comes down in lumps or as a granular mass, the colouring matters being then unequally fixed and the lakes forming sandy, non-coherent masses when dry. If the azo colour is very sensitive—*e.g.*, cotton scarlet—the lake easily turns brown in shade, more especially when the colouring matter has to be boiled a long time during fixation. Instead of caustic lime pure levigated chalk is often preferable, which, on account of its constant composition, is more convenient and reliable in working, and therefore gives uniform results.

Besides these three principal methods of precipitation, other processes are used with red azo colours, but are of little importance, and therefore need merely be mentioned here. One of these methods is the so-called "phosphoric acid precipitation," which, as already mentioned on p. 485, is based on the formation of aluminium phosphate. Another is the formation of barium carbonate from soda and barium chloride, the colouring matter being precipitated at the same time. This last method has, however, the disadvantage that the colouring matter is kept in contact with a solution of free soda for some time, so that, in consequence of the sensitiveness of many azo colours to alkalies, the brightness of the lakes is impaired.

Finally it may be mentioned that the lakes made by the above methods can be made much brighter by repeated washings. Hence this operation should never be neglected, especially since most azo-colour precipitates are fast to water, and facilitate the washing process by settling down quickly.

As to the *simpler scarlet lakes*, all the brands of scarlet, now sold by the colour-makers in nearly identical brightness and strength, are suitable, either alone or mixed in any desired proportion. The resulting lakes, when made by the same method, always exhibit identical physical properties, except for small differences with regard to shade and brightness. The manufacturing process being easy when the above-mentioned rules are observed, there is no difficulty in matching a given sample, since a distinct system of classification according to shade prevails in the trade, viz., scarlet G, 2G, scarlet R, 2R, 3R, 4R, 5R, and 6R, the letter G indicating the yellowish brands, R the reddish ones, and the numerals 2, 3, &c., the progressive depth of shade (in the same way B is used for bluish brands). Of these brands, scarlet GG, G, R, 2R, and 3R can be easily and completely precipitated by barium chloride in any proportion or method, though the lakes are always of a rather more bluish tinge than the solution of the colouring matter, viewed by transmitted light, the most noticeable instance being afforded by the lakes from scarlet 3R. Scarlet 4R, 5R, and 6R, however, present great difficulties in the way of complete precipitation, even when special precautions are adopted. Scarlet 4R gives inferior lakes. Scarlets 3R to 6R diminish considerably in brightness as the bluish tone increases, and the lakes, therefore, are considerably dearer. These brands of scarlet being also more expensive than the yellow ones, it is easy to understand why they are seldom used for making lakes.

Besides these ordinary brands of scarlet, most aniline colour firms produce so-called *scarlets for lakes*, which, as the name implies, are easily and completely precipitated. A discussion of these very numerous types of this group of azo colours is impossible here, more particularly since the colour-makers will give all necessary particulars if desired.

The red azo colours, known in the trade as *croceines*, are more difficult to precipitate than those mentioned hitherto. This group includes the *scarlets* (Ecarlates) and the various *cotton scarlets*. These colouring matters are not only more powerful, but also more sensitive to high temperatures and the salts used for precipitation. Precipitation is therefore seldom complete except in the cold (20° to 30° C.), and after prolonged stirring, sometimes for days. Their greater tinctorial power also entails a sometimes considerable variation in the proportion of the raw materials, so that the precipitation may become very complicated and troublesome, the more because the brightest shades are only obtained by using very dilute solutions.

The simple alumina and barium chloride process is generally insufficient for fixing these azo colours, complete precipitation being generally out of the question, and even when obtainable the lakes are more of a brownish tone than pure red. This may be due to the proportion of alumina in the mixture with artificial barytes being too large to permit the colouring matter to be properly combined, a further addition of barium chloride being needed to throw down the excess of colouring matter.

This circumstance would also explain the brown tone of such lakes; but, on the other hand, it must be remembered that some croceines cannot be completely fixed even when a definite quantity of Glauber salt is added to the solution of aluminium sulphate in order to adjust the ratio between the alumina and artificial barytes. This disadvantage, however, does not occur when precipitation is effected by the alum and barium chloride method, because, though this process may be no less troublesome, still the colouring matter is fully precipitated after prolonged stirring. Moreover, if suitably diluted solutions have been used, the resulting lakes are always of a pure red tone, brown-coloured precipitates occurring only when the precipitating solutions have been used too hot or too strong.

Still greater difficulty is met with in precipitating the so-called *chromotropes*. Of this group, only chromotrope 2B, 6B, and 10B can be successfully precipitated, and furnish more or less suitable lakes. *Chromazone reds* behave in a very similar manner in regard to precipitation, and are only precipitable in certain definite proportions. Usually they have to stand for three to four days, and be stirred until the filtrates are only slightly tinged with blue or red.

Of the recent azo colours, *brilliant carmine, astacine red, carminogen, heli purpurin,* &c., are of special importance, and can mostly be successfully precipitated with barium chloride by one or other of the methods named. *Bordeaux* and *amaranth reds* behave in a similar manner, but are now seldom used for lakes, on account of their low intensity and the poor tone of the precipitate with barium chloride.

The *insoluble azo colours*—the *pigment colouring matters*, as they are called by some makers—on the other hand, are becoming more popular, though rather difficult to work up into lake pigments. The number of these colours is now very considerable, and their shades range from the palest sulphur yellow to the darkest bluish crimson. The most important are:

1. *Farbwerke Höchst, late Meister Lucius und Brüning.*
   - Pigment chlorine GG.
   - Pigment chrome yellow L.
   - Pigment orange R.
   - Pigment red G and B.
   - Pigment purple A.
   - Pigment crimson R, N.
   - Red for Lakes P and C.

2. *The Badische Anilin- und Soda-Fabrik, Ludwigshafen.*
   - Autol orange.
   - Autol red GL, RLP, BGL, RLP bluish, BL.
   - Lithol red, lithol red GG.

3. *Farbenfabriken, late Fr. Bayer und Co., Elberfeld.*
   - Helio purpurin, 3BL, 5BL.
   - Helio fast red G.

4. *A. G. für Anilinfabrikation, Berlin.*
   - Red for lakes 4644

All these coal-tar colours are sold by their makers in the form of a past containing variable proportions of dry matter, and are all very slightly soluble in water, if at all. For the production of lakes they are mixed with suitable carriers by purely mechanical means, either at ordinary temperature in edge runners, wet mills, cone mills, &c., or made into a paste with water, added to the carrier through a sieve, and the mixture boiled with a definite quantity of barium chloride. In the latter method the lakes acquire a somewhat higher covering power; but some colouring matters undergo a change of shade at high temperatures or when treated with barium chloride, turning darker and more bluish (*e.g.*, red for lakes P and lithol red) or brownish (pigment red G). The greatest intensity of these lakes is, however, unattainable by any of the methods given, but is produced only after a repeated and sometimes very powerful grinding of the dry lakes.

The lakes from these insoluble azo colours are used not only for litho and letterpress printing, water colours, &c., but also as varnish or oil colours, according to the material chosen as the carrier. These lakes are mostly bright colours of good covering power, fast to alkalies, alcohol, and generally to light as well.

Though, as already mentioned, most aniline colour works put special azo colours on the market as so called "scarlets for lakes," some of which give very bright scarlet lakes when precipitated by barium chloride alone, as described, they are mostly used to mix with differently shaded scarlet or orange colouring matters of the azo class. Scarlets for lakes are generally somewhat dearer, their lakes are distinguished by a cold, bluish tone, and finally they are too few in number to furnish a complete series of scarlet lakes. Apart from the fact that the higher price of scarlets for lakes necessitates suitable additions of cheaper ordinary scarlets, it is also advisable to employ more yellowish scarlets, or even pure azo oranges, in order to obtain bright, warm tones and suitable gradation along the scale. The aniline colour-makers would therefore be obliged to keep a large number of various brands of scarlet in stock, were it not that, fortunately, the scarlet lakes, by their brightness and other properties, are able to furnish a series of uniform lakes by suitable mixtures of a small number of yell[illegible] and bluish scarlet colouring matters.

This fact is best illustrated by an example. Assuming the following ratios of raw materials to be taken for the manufacture of scarlet lakes:

20 aluminium sulphate, 1 : 10
10 calcined soda, 1 : 10
15 colouring matter, 1 : 50
37·5 barium chloride, 1 : 20

then, in accordance with this table, a whole series of variously shaded lakes can be obtained from scarlet 4GBL and scarlet 2RL, the other properties of these lakes remaining constant, on account of the regular proportion maintained between aluminium sulphate, soda, and barium chloride.

The quantities of colouring matters, for instance, may be as follows:

Scarlet Lake	A (very yellowish).	B (yellowish).	C (reddish).	D (red).	E (bluish).	F (very bluish).
Aluminium sulphate	20	20	20	20	20	20
Calcined soda	10	10	10	10	10	10
Scarlet 4GBL	15	12	9	6	3	—
Scarlet 2RL	—	3	6	9	12	15
Barium chloride	37·5	37·5	37·5	37·5	37·5	37·5

Exactly the same lakes can be obtained by other mixtures of red azo colours—for instance, orange II and scarlet 2RL—if the shade and intensity of scarlet 4GBL has once been determined by mixing these colouring matters in definite quantities, and it is easy to calculate the weights required to obtain the other lakes, B, C, D, &c. If, for instance, it is found that a mixture of 4 parts of orange II and 1 part of scarlet 2RL produces exactly the same shade and intensity as 5 parts of scarlet 4GBL, then lake A can be prepared from the following weights:

Aluminium sulphate	20
Calcined soda	10
Orange II	12
Scarlet 2RL	3
Barium chloride	37·5

12 parts of scarlet 4GBL having been used to obtain lake B, the formula for the new colouring matter is:

4 orange II : 5 scarlet 4GBL = x : 12.

Hence $x = \frac{48}{5} = 9{\cdot}6$ orange II; viz., scarlet lake B is obtained of the same shade and intensity if 12 parts of scarlet 4GBL are replaced by 9·6 of orange II and 5·4 of scarlet 2RL for precipitation. In the same way, for lake C the quantities of colouring matter are 7·2 parts of orange II and 7·8 parts of scarlet 2RL; and since orange II is cheaper than scarlet 4GBL, the resulting lakes are also cheaper.

These combinations can be varied all through the series of these lakes. Thus, for instance, scarlet for lakes GG can be taken instead of orange II in substitution for scarlet 4GBL, and at the same time scarlet 3RL can be replaced for certain lakes of the series by a corresponding quantity of a more yellowish azo colour, such as scarlet R, or throughout the whole series by a more bluish product—*e.g.*, scarlet B extra. In a similar manner, various combinations can be arranged between the different brands of scarlet and orange on the one hand and all the scarlet and Bordeaux colouring matters or insoluble azo colours on the other. The number of possible shades varies, of course, inversely with the relative approximation of the colours used in the combination. At the same time, however, any change in the colouring matters used is accompanied by an alteration in the cost of the lakes. This is not the place for discussing the point, and it must therefore be left to the skill and judgment of the colour-maker or chemist for decision in each case.

The method of dissolving the colouring matters to be precipitated together is of special importance with regard to the brightness of most lakes from azo colours. The colouring matters can be dissolved simultaneously or one after the other. In the latter case the separate solutions can be added to the precipitation mixture in various orders. Experience teaches, however, that lakes are generally much brighter when the colouring matters have been dissolved together, though in many cases there are also accompanying disadvantages. The colouring matters may always be dissolved together if of the same chemical nature; otherwise care is advisable, and the results furnished by the joint and separate solutions must be compared. If the former prove unsuitable, the order in which the separate solutions are to be run into the precipitating tank must be ascertained, so as to avoid the same disadvantage as would ensue from joint solution. This disadvantage chiefly consists of a typical property possessed by some colouring matters—namely, that of precipitating one another from solution, on account of differences in their chemical nature. This, of course, prevents joint solution. Though this disadvantage is rarely encountered with acid colouring matters, it often happens that in the presence of dissolved salts, such as are always present in the precipitation liquor, the colouring matter is precipitated from the solution in a powdery or crystalline state. This is not a true precipitation, and sometimes occurs on mixing solutions of acid colouring matters, if the one colouring matter is more sparingly soluble in water than the other, and if sufficient allowance has not been made for this in fixing the temperature and the quantity of water used. Many recent azo colours, for instance, dissolve only in very hot water, and fall down more or less completely when mixed with cooler solutions of other azo colours, and if this happened in the precipitating tanks the effect of the colouring matter in question would be entirely spoiled. No definite general rules can be given here respecting the order in which the solutions should be added to the carrier, the number of combinations being too great; these remarks being intended solely to explain the frequently occurring phenomenon in question.

d. Violet Lakes from Acid Coal-Tar Colours

Though very bright violet lakes can only be obtained from basic coal-tar colours, acid violets, especially derivatives of the azo group, are now generally preferred, on account of their greater fastness. They are very few in number, only two kinds being known—ordinary *acid violet* and *fast acid violet*, all the brands of which are used for lake-making. They are precipitated without any special difficulties by the various barium chloride processes used for scarlet lakes (*q.v.*). They are very expensive, especially the reddish brands of fast acid violet, and this, coupled with their low colouring power in comparison with basic violet colouring matters, accounts for their lakes being used only for special printing purposes.

e. Blue Lakes from Acid Coal-tar Colouring Matters

Between the pure violet and the blue acid colouring matters are several which give bright lakes of a bluish-violet or reddish-blue tone, and are specially suitable for printing inks—*formyl violet S4B* (Cassella) and *guinea violet 4B* (Berlin). They are precipitated completely by any of the barium chloride methods, and produce very bright, though rather pale, lakes, absolutely fast to water.

The number of pure blue acid colouring matters is very large in comparison with the violets, and their use for lake-manufacturing is therefore far more important. The shades of lakes obtained from these colouring matters range from the palest sky-blue to the deepest indigo. They are easily manufactured, most of the colouring matters belonging to this class being easily and completely precipitated in any desired proportion by barium chloride

Each brand, moreover, furnishes a suitable lake, and therefore the complicated mixtures required for scarlet lakes are rarely necessary. The range of tones possible with these colouring matters is limited on the one hand by *patent blue* (xylene blue), which gives the lightest shades, and on the other by *helio fast blue*, producing the darkest indigo tones, intermediate shades being obtained from the brands known as cotton blue, water blue, cloth blue, light blue, cotton light blue, opal blue, deep blue, Chinese blue, pure blue, navy blue, plain blue, wash blue, &c., and supplied in identical quality by nearly all aniline colour makers.

The blue lakes can be used for all purposes and be prepared by nearly all the methods of precipitation by barium chloride. With a few exceptions, the results of these various precipitation methods are the same with regard to the quantity obtained and brightness. Some brands of patent blue are more difficult to precipitate than the other blue acid colouring matters, but in most cases a complete precipitation can be effected after prolonged stirring, a shorter method sometimes practicable being that of after precipitation with aluminium sulphate, soda, and barium chloride, as already described.

f. Lakes from Green Acid Colouring Matters

The few green acid colouring matters—*acid green* and *naphthol green*—are the most difficult to precipitate of all the acid colouring matters. Most of the barium chloride precipitation methods either fail to give complete fixation of the colouring matter, or require the adoption of special artifices to ensure success. This is specially the case with naphthol green, which requires a prolonged stirring or standing of the liquids before it can be precipitated at all, and then only in an imperfect degree in comparison with acid green. Barium chloride alone is an imperfect precipitant of either of these colouring matters, though better in the case of acid green than with naphthol green, the brands of this latter from different works having quite a different behaviour toward barium chloride. The alumina soda method is the most suitable of the various combined methods of precipitation, but must often be modified according to the kind of colouring matter used. The usual modification consists in mixing the aluminium sulphate with the solution of the colouring matter *i.e.*, the reverse of the usual method—then precipitating with barium chloride, and converting the aluminium chloride into aluminium oxide with soda. Even with this method, and especially if considerable quantities of colouring matter are treated, a complete precipitation of the colouring matter is seldom obtained, an after-precipitation with aluminium sulphate or barium chloride, or both together, being usually necessary, even after prolonged stirring. The resulting acid green lakes have usually a bluish-green tone, and are sold as *viridin greens*. In spite of their deficient fastness to water, they must be washed repeatedly, since otherwise they dry hard and sometimes lose their brilliancy. In the manufacture of these lakes both the precipitation temperature and the degree of dilution play a considerable part. No distinct rules, however, can be given, the nature of the various brands of colouring matters, which, of course, is a determinative factor, being often very different. Generally, however, the result will be more favourable in proportion to the degree of dilution of the solutions and the lower the precipitation temperature.

To a still greater extent the less bright, rather moss-green coloured naphthol green seems to depend for complete precipitation on definite quantities of barium chloride, aluminium sulphate, and soda, an excess not being precipitable by barium chloride alone. The number of possible shades of viridin greens, as well as of lakes from naphthol green, would therefore be relatively small, were it not possible to increase them by simultaneous precipitation with additions of quinolin or naphthol yellow. By this means, and given definite proportions, a considerable number of suitable viridin greens can be obtained in all tones from the lightest canary green to the deepest grass green, which in point of intensity, brilliancy, and permanency can hardly be obtained by combining yellow and green lakes in any other way.

Mixed lakes from naphthol green and quinolin yellow are less often met with, but the production of combined lakes from naphthol yellow, paper yellow, and astacine yellow with naphthol green has considerably increased. These lakes not only exhibit very agreeable olive-green shades, recalling (especially in their lighter shades) the chrome greens, but also possess other very useful properties, especially great fastness to light.

II. Colouring Matters Precipitated by Lead Salts

Though the group of resorcin colouring matters, which here has to be taken into consideration, is small, they furnish a considerable series of very bright lakes, which play a part no less important than, for instance, the far more numerous azo-colour lakes. In consequence of the complete precipitation of the resorcin colours with lead salts upon an opaque base by a very simple process, these lakes have the advantage of forming pigment colours of good covering power, and are used especially for varnish painting - a feature comparatively rare in many lakes, *i.e.*, under special conditions only.

Resorcin colouring matters are also of special importance to wall and fancy paper lakes, the special lakes - chiefly *pink lake* and *imitation carmine lake*—used for these purposes being unobtainable in such bright and pure shades from other coal-tar colours of similar shade, though their fastness to light and the other properties are not very high.

Lakes from resorcin colours are principally used in the form of the so-called *geranium lakes*, produced in a great variety of shades, and used as transparent and opaque colours of great covering power in all branches of the printing industries.

Resorcin colour lakes for ordinary painting are sold as *vermilionettes* (royal reds, imitation vermilion, &c.) in a great variety of shades. They have in many cases replaced the natural and artificial vermilion as painter's colours, on account of their greater brilliancy and cheapness.

The group of resorcin colours is formed by *eosine*, *erythrosine*, *phloxine*, and *rose Bengale*, sold by makers under the same names and in nearly the same quality. The eosine forms the yellowest brands, rose Bengale the bluest types of this group. They are completely precipitated by lead acetate or lead nitrate, the brilliancy of the precipitates being the same in most cases. The precipitation is very easy, the solution of the colouring matter being mixed with the carrier, and the dissolved lead salt afterwards added, with constant stirring. The precipitation is always complete when equal quantities of colouring matter and lead salt are used, and the top liquor will then be quite colourless. Neither the degree of dilution nor the temperature of precipitation seems to have much influence on the brilliancy of the resulting lake, though a suitable impure carrier, especially when considerable quantities of colouring matter are being treated, may precipitate the colouring matter in such a way that the dry lake is of a brownish tinge with a more or less metallic lustre when applied as an oil paint, both these features being regarded as defects.

Eosine lakes for wall and fancy papers contain as carrier aluminium hydroxide, artificial barytes, barytes, starch, china clay, white brands of clay, &c., alone or mixed together in any desired proportion.

Red lead with small quantities of barytes or lead sulphate is almost exclusively used as a carrier for vermilionettes, alumina and orange lead being used for the finer sorts, in order to diminish their high specific gravity. Besides the more or less bluish or yellowish shade of the eosine colouring matter, the carrier—*i.e.*, the quantity and the natural colour of the materials employed for this purpose—also modify the shade of the product.* All the resorcin colours can be mixed together in any desired proportions, and also be dissolved together and precipitated on the carrier by the same lead salt without impairing the brilliancy of the lakes.

A more complicated process is necessary for making geranium lakes, the higher commercial value and finer uses of which require greater care in the manufacture. Alumina, artificial barytes, and lead sulphate form the chief carriers, starch, red lead, or white clays being more rarely used. The prepared carriers are (as already described) mixed with the hot solutions of colouring matter, and the colouring principle is precipitated by the solution of lead salt, with constant stirring. Geranium lakes are made not only from all resorcin colours, but also from the eosines, particularly erythrosine and phloxine (rarely rose Bengale), red azo colours, like orange II, and all scarlets. The latter colouring matters are specially used when the geranium lakes are desired to produce bright oil paints. In this case an orange or scarlet lake from aluminium sulphate, soda, and barium chloride is first made in the usual way and sufficiently washed; the solution of resorcin colour is then added, and finally precipitated by the lead salt solution. In this way a great variety of shades of very bright geranium lakes can be obtained. Where large quantities of colouring matter have to be treated, as is particularly the case with very bright lakes, the geranium lakes are often found to "bronze" more or less when painted with oil or printed. To avoid this defect, due to a partial precipitation of the eosine acid by free acetic or nitric acid during the treatment of the resorcin colour with the lead salt, it is advisable to add a small quantity of alkali (caustic soda) to the solution of colouring matter, so as to neutralise the acetic or nitric acid before eosine acid can be formed.

Pure eosine acid (bromofluorescein) will also furnish lakes which "bronze" to a high degree (the so-called bronze-red lakes), and are therefore specially suitable for printing purposes. Eosine acid is dissolved by boiling with alkali carbonates (soda), the acid being reprecipitated in a finely divided state by mineral acids (sulphuric acid), then transformed into lead eosinate by means of lead acetate, and finally mixed with a thin paste of freshly precipitated alumina. The lake is then washed several times, and finished in the usual way.

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* The lead salts used for precipitation have also a shading influence on the resulting lakes, acetate of lead always producing more yellowish pigments than nitrate of lead. [TRANSLATOR.]

Ordinary geranium lakes are very sensitive to the influence of spirit varnish, but can be greatly improved by the use of sodium aluminate. The solution of colouring matter, mixed with aluminium sulphate, is first treated with lead nitrate, and afterwards with an aqueous solution of sodium aluminate; or the two solutions are united, and the precipitate of lead hydroxide and alumina is added with the solution of sodium nitrate to the solution of colouring matter. The precipitation is very complete.

III. Coal-tar Colouring Matters Precipitated by Tannic Acid

The very large class of *basic* coal-tar colours especially have the property of forming tannates, which are insoluble in water. This method of precipitation is one of the most important used, though it is not suitable for all basic coal-tar colours, some of them giving tannates of poor colour and instable character. In view of the great intensity and the bright colour of the basic coal-tar colours, and the ease with which they are completely precipitable from aqueous solutions by weak organic acids or similar bodies, it was quite natural that other methods of precipitation besides that by tannic acid should be gradually introduced, since these methods, though they cannot be used with all basic coal-tar colours, furnish with some types better results than the tannic acid process.

The following basic coal-tar colours are generally used for manufacturing lakes: The various brands of magenta and their cheaper by-products, like cerise, maroon, grenadine; new magenta; the various brands of methyl violet, brilliant green (ethyl green, diamond green, &c.), malachite green (solid green); auramine, safranine, rhodamine, rhoduline, vesuvine (Manchester brown, Bismarck brown, &c.), Victoria blue, methylene blue, methylene violet, methylene green, &c.

Basic colouring matters are mostly very sparingly soluble even in pure water. Water containing calcium carbonate or magnesia decomposes most colouring matters, insoluble resinous colour bases being produced. Therefore water of condensation, free from lime, and at a temperature of about 70° to 80° C., is mostly used, the quantity required being 200 to 250 times that of the colouring matter. If no water of condensation is at disposal, the colouring matters are treated with about a fivefold quantity of acetic acid of 8° B. strength (according to the instructions issued by the Höchst Farbwerke, late Meister Lucius und Brüning), hot water at 70° to 80° C. being afterwards added by degrees. Another very suitable practice is to mix the colouring matters with a twofold quantity of anhydrous glycerine and a fourfold quantity of alcohol on the water-bath, the whole being then dissolved in hot water.

The most important methods of precipitating basic colours may be classified as follows:

a. Precipitation with tannic acid.
b. „ „ soap or Turkey red oil.
c. „ „ resin.
d. „ „ casein or albumen.
e. „ „ sodium phosphate, arsenic, or sodium silicate

Particulars of the chief carriers and colours will be given in describing the precipitation methods, to facilitate comprehension of this somewhat complicated subject by the reader.

a. Precipitation by Tannic Acid

Tannic acid, $C_{11}H_{10}O_9 + 2H_2O$, the properties and manufacture of which have been described on p. 337, is sold in various kinds and qualities, according to the uses for which it is intended. The better kinds are obtainable as a loose, pale yellowish powder, the purest form being the nearly colourless flake tannin—the only quality suitable for manufacturing lakes.

The alkaline solutions of tannin easily absorb oxygen from the air and darken in colour; aqueous solutions soon grow mouldy. In the dry state also tannic acid is liable to change when exposed to the air, and must therefore be kept in tightly closed bottles. Tannin is a monobasic acid, and completely, in spite of its slightly acid properties, decomposes many carbonates, especially alkali carbonate (soda). When boiled with dilute acids it is converted into gallic acid, and conversely is obtained from the latter by the aid of oxychloride of phosphorus, water being formed:

$$\underbrace{2C_7H_6O_5}_{\text{Gallic acid}} = \underbrace{C_{11}H_{10}O_9}_{\text{Tannin}} + H_2O.$$

Tannin is therefore the anhydride of gallic acid—digallic acid.

The action of tannic acid in the manufacture of lakes is based upon its property of forming with colour bases tannates, that are nearly or quite insoluble in water. These tannates are precipitated in such a fine state of division that they cover the single particles of the base completely. The resulting mechanical mixture appears, therefore, as a uniformly coloured pigment. The nature of the carrier also plays an important part—as with all lake pigments—since, apart from their influence on the more or less brilliant shade of the resulting lake, the various carriers considerably influence the precipitation of the colouring matter. Consequently the quantity of tannin used for precipitation varies also according to the nature of the carrier.

Tannin is seldom used alone as a precipitant, the resulting precipitates being rather dull and of little or no value. The same applies to lakes precipitated with sodium stannate. The full effect of tannin as a precipitant is only obtained when tartar emetic* is used at the same time.

The most simple method of precipitation is as follows: The carrier is first mixed with water, the solution of colouring matter being added and, with constant stirring, precipitated by the requisite quantity of tannic acid dissolved in water. If siliceous materials like china clay, green earth, ochre, diatomaceous earth, &c., partly or entirely constitute the carrier, a corresponding quantity of the solution of colouring matter will be absorbed without any precipitating agent, and only the more or less considerable surplus has to be precipitated, the requisite quantity of the precipitating medium depending on the quantity of the said ingredients in the carrier. With inert carriers like barytes, artificial barytes, lead sulphate, lithopone, &c. (according to the nature of the colouring matter chosen), some colouring matters can be precipitated by tannic acid alone, but in most cases an addition of sodium acetate, soda, or tartar emetic, which saturate the acidity of the colouring matter (liberated by the tannic acid), will be necessary. It is advisable to use tartar emetic for another reason: the resulting lakes are faster to alcohol, which readily and completely dissolves all basic coal-tar colours. Hence the tannic acid and tartar emetic method is specially recommended for all lithographic, printing ink and varnishable lakes. The latter property, however, is possessed by only a few basic lake pigments, and even not always entirely.

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* Or antimony lactate or bilactate. See remark on p. 290. [TRANSLATOR.]

Tannic acid is not always an entirely suitable precipitating agent for lakes from all basic coal-tar colours with regard to brightness and brilliancy, some of the lakes being deficient in colour, dull, or even completely discoloured, especially those from the violet and blue basic coal-tar colours. The method is, however, the more important in the manufacture of green and red basic lakes, which cannot be obtained in such brilliant, pure shades by any other process. The chief colouring matters used for this purpose are brilliant and malachite green, the various brands of magenta, also cerise, maroon, grenadine, rhoduline, &c.

b. Precipitation with Soap or Turkey Red Oil

This method is based on the double reaction of colour bases with oleic, stearic, and palmitic acids to form corresponding insoluble salts, which are mostly very bright in shade, and, in consequence of their fine division, envelop carriers like the tannates. The character of the soap and the saponifiability of the oils used for precipitating purposes are the principal factors determining successful results. The soap must not contain any free alkali, which always causes a considerable loss of colouring matter or unfavourably changes the shade, and therefore Marseilles soap is preferred, the usual proportions being equal quantities of soap and colouring matter. For this purpose the carrier is first mixed with water, the solution of the colouring matter being added afterwards. The soap, dissolved in warm water, is then stirred in very slowly, the success of the result being usually facilitated by boiling. This method is especially used for precipitating violet and blue, rarely red, basic coal-tar colours. Soap is very often replaced by Turkey red oil, which is diluted with ten volumes of water, and added to the mixture of carrier and colouring matter. The precipitation is usually complete, and if not can be made so by small additions of tannic acid, zinc or tin salts. The latter treatment is applied when very bright lakes are desired—*i.e.*, large quantities of colouring matters and oil are being worked. To avoid excessive greasiness of the dry lakes in such cases the quantity of Turkey red oil is restricted to that necessary for precipitation, and the remainder is replaced by a suitable quantity of the bodies mentioned.

c. Precipitation by Aid of Resin Soap

Though all basic coal-tar colours form very bright lakes* with resin soap, and though this method is a very convenient and reliable one, it is only seldom used, the lakes having many detrimental properties which prevent their extended application, more especially the ready solubility in alcohol and a disagreeable tendency to froth when being used for making wall- and fancy papers. Some of these lakes also "bleed" when mixed with size, and stain through the paper on which they are printed—faults which exclude their use for many purposes. Pure resin lakes are therefore rarely manufactured, but the method is combined with others, which minimise the defects just alluded to, if they do not entirely cure them.

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* This species of lake can, in general, be easily recognised by the experienced colour man on account of the peculiar brilliancy and warm hue. [TRANSLATOR.]

The colouring matter, mixed with an alkaline solution of resin, is precipitated by salts of zinc or alumina, or both together, a resin soap being formed. It is doubtful whether the reaction is one of precipitation, or merely an absorption of the colouring matter by the resin soap produced in an insoluble form by the said salts. There is, however, a good deal of evidence in favour of the latter hypothesis.

To produce the alkaline solution of resin, powdered light colophony is treated with a moderately strong solution of soda or dilute caustic soda at boiling heat, until the resin is entirely dissolved. Generally 1 part of calcined soda is taken to 4 parts of pure colophony, and the solution is best prepared in a copper vessel over a fire. The following proportions of raw materials and water may be recommended:

2 cwt. colophony, best brand.	2 cwt. colophony.
½ cwt. calcined soda.	¼ cwt. calcined soda.
44 galls. water.	13¼ galls. caustic soda (four times standard strength), 110 galls. water.

The quantity of alkali depends entirely on the quality of the colophony, the above figures being therefore subject to alteration. For obvious reasons any considerable excess of alkali must be avoided, and therefore caustic soda is not specially suitable. This solution of resin must be diluted with water in suitable proportions, according to the nature of the colouring matter to be precipitated.

After the material to be coloured is mixed with water the solution of the colouring matter is added, followed by the resin solution, which is slowly and well stirred in, and the whole is then heated to boiling. Some colouring matters will be precipitated at once, whilst others remain quite inert. Complete precipitation is effected by a solution of zinc sulphate or alum, or both together, but usually it only takes place in a satisfactory manner when the mass is becoming quite cold. Continued stirring is essential, especially if alum is used partly or wholly in the precipitating medium, as this substance generally causes a most inconvenient degree of frothing. If insufficiently stirred the precipitate very often separates from the carrier, or —when the heating was not sufficient or has been stopped too soon—the resin falls down as a sticky mass.

The chief carriers are especially alumina, artificial barytes, white and coloured clays, seldom barytes or gypsum. The lakes from resin soap are used for wall- and fancy paper making, but only matt varieties, as they will not stand calendering. The best lakes of this kind, the so-called *resinate lakes*, are obtained from auramine, rhodamine, magenta, and patent blue P.

d. Precipitation with Casein or Albumen

This method of producing lakes is the least investigated and applied, though, according to reports in the technical press, it furnishes lakes that are both very bright and peculiarly fast to water. For this purpose a cold ammoniacal solution of casein is mixed with the dissolved colouring matter (albumen being used as a very dilute aqueous solution), the carrier is incorporated with this mixture, and is afterwards precipitated completely by slowly heating to 86° to 90° C., the precipitating medium coagulating. According to Dr. C. O. Weber (*Färberzeitung*), when a solution of patent blue P is treated with a solution of egg albumen it is found that even with a great excess the colouring matter is not precipitated completely. However, on adding a few drops of acetic acid to the mixture the brightly coloured albumen lake of patent blue is completely precipitated if the mixture be heated to 80° to 90° C. To precipitate brilliant green by this method, 10 grms. of egg albumen are dissolved in water, the solution is filtered, made up to 1000 c.c., and mixed with the carrier. A solution of 0·5 grm. brilliant green, 5 c.c. of acetic acid (80 per cent.), and 5 grms. of sodium acetate (in 100 c.c. of water) are then added. On heating the originally clear mixture to 86° C. the colour gradually becomes turbid, and finally, by prolonged heating, a very bright green lake settles down in the form of coarse flakes.

The other basic colouring matters exhibit the same behaviour, though the brightness and completeness of precipitation differ, of course, with the various colouring matters.

Moreover, the above method of manufacturing albumen lakes is applicable to all basic and acid coal-tar colours, as also all basic sulphone colours, the azo colours and nitro-sulphone colours. This fact, which is important to the colour-manufacturing industry, merits closer investigation, especially since the lakes are very fast to light.

These groups of coal-tar colours behave in the same manner toward a solution of casein, obtained by dissolving 10 parts of casein in 100 parts of water, followed by digestion with 1 to 1·5 parts of ammonia at 40° C. Here also, however, the precipitation must be completed by the aid of variable quantities of solution of stannic chloride. These lakes will mostly stand water, the only essential feature being a suitable and possibly neutral solution of casein. Only just as much of the stannic chloride solution is added as is needed to precipitate the colouring matter. Any other acid salts, such as aluminium chloride, stannic acetate, aluminium acetate, &c., can be used in the place of the tin salt mentioned. The method is of special importance for manufacturing lakes from rhodamine and eosine colouring matters, which are in this special case not poisonous.

e. Precipitation with Sodium Phosphate, Arsenic, or Sodium Silicate

These methods of precipitation have already been fully described on pp. 484 and 485. They are chiefly confined to the manufacture of violet lakes from methyl violet, sodium phosphate being the best precipitating agent for this purpose. The method is based more particularly on the formation of double compounds of aluminium phosphate and phosphates of the colouring matters, and therefore the carrier must chiefly consist of aluminium hydroxide. The sodium phosphate and arsenic precipitations are mostly incomplete, though considerably improved by continual stirring, or by standing for a certain time. Silicates,* especially sodium silicate, potassium bichromate or neutral chromate are sometimes employed in making lakes from basic coal-tar colours, but these methods are of small technical importance.

In consequence of their chemical nature, the basic coal-tar colours have the property of forming insoluble compounds with acid colouring matters—*i.e.*, of precipitating these later. This property is sometimes utilised if the colouring matters to be precipitated are not of directly opposite tints, but fast lakes of this kind are very difficult to prepare, and when obtained by this method of precipitation are generally not at all fast. For this reason only a few of these combinations have survived, on account of especial brightness or characteristic tone. Eosine colouring matters and magenta (rubine) or rhodamine, azo orange brands and scarlet with magenta, brilliant green and methyl violet (maroon, and leather lake), and yellow acid colouring matters with methylene blue or methylene violet (olive-green lakes) are chiefly used for this purpose. These lakes will be described more fully when dealing with the combined lakes.

IV. Colouring Matters Precipitated Direct by Siliceous Materials

The capacity of many native siliceous minerals and earths—green earth, bole, china clay, silica earth, ochre, umber, white and coloured clay, &c.—for absorbing certain quantities of coal-tar colours without any precipitating media is largely utilised in modern colour-making for manufacturing ordinary painter's colours, especially for lime washes. The basic coal-tar colours give the best results with regard to the tone and fastness of the lakes. The colouring matters most used are *auramine, chrysoidine, vesuvine, magenta (cerise, grenadine, maroon), malachite green, brilliant green, methyl violet, Victoria blue, methylene blue, safranine, rhodamine*, &c., applied alone or suitably mixed.

When the said earthy minerals are levigated in contact with the solutions of these coal-tar colours, the latter are generally absorbed immediately, and fixed so strongly as to resist even the most powerful alkalies. This absorption forms the basis of the application of these lakes as "lime colours." The silica in the carriers is believed to fix the colours in consequence of the formation of insoluble silicates and double silicates. The accuracy of this opinion is proved by the variable combining power of one and the same material for different colouring matters, or, conversely, of one and the same colouring matter toward the different carriers, according to their content of silica. Thus a certain kind and quantity of green earth will not take up the same quantity of auramine and brilliant green as it does of magenta, methylene blue, methyl violet, &c.†

The method is practised in a most simple way. The carrier is mixed with water, and the solution of colouring matter is added, with continual stirring, until the desired shade and intensity are obtained. The manufacture of these mostly very cheap "lime colours" being only profitable when worked on a large scale, plants of corresponding size are required. The levigation of clayey carriers, which are difficult to work, is effected in large shallow square tanks let into the ground, the powdered materials being treated with water and worked with iron crutches until a fairly stiff paste is obtained. On adding the solution of colouring matter the mass usually swells up considerably, and is difficult to work in the manner absolutely necessary to ensure equal division of the colouring matter, so that in many cases an addition of large quantities of water becomes indispensable. Excessive dilution of the colour paste must, however, be avoided, and, owing to the great trouble and expense of filtering and pressing, the mass must be kept of such a consistency that it can be shovelled out of the tank and on to the drying boards without running. Drying is performed in the open air or of sheds protected from the rain, the dry mass being afterwards ground in edge-runners or suitable mills.

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* Or silicates and certain vegetable extracts—*e.g.*, quercitron extract, &c. [TRANSLATOR.]

† It may be mentioned that the various colouring matters are not bound on the same materials with the same strength. Green colouring matters, for instance, produce faster lakes with the same raw materials than red ones; the chemical binding, therefore, must be stronger than with red colouring matters. [TRANSLATOR.]

The fixation of the colouring matter is mostly complete at the ordinary temperature, though for producing finer and dearer lime colours heat can be advantageously applied and the mass kept more dilute, this treatment facilitating complete fixation and giving brighter lakes. A good deal depends on the nature of the carrier, heating being inadvisable when it contains calcium or magnesium carbonates in addition to silicates, since in such case the colour bases may be partly thrown down in a more or less uncoloured state, so that a loss of colouring principle is incurred. This result can, however, be partly or entirely counteracted by the addition of a suitable quantity of sulphuric, hydrochloric, or acetic acid.

The Combined Lake Pigments

Before discussing other matters of precipitation it will be advisable to acquaint the reader with the most important combinations obtainable by the methods already described. Though the subject is too broad to be treated thoroughly, a few typical examples may be given, which, if properly arranged and explained, will facilitate independent experiment.

The combined lakes (*mixed lakes*) can be classified into two principal groups:

a. Lakes obtained by the joint or separate precipitation of colouring materials of identical, or nearly identical, chemical nature, but of various shades—*e.g.*, *scarlet lakes* from variously shaded orange and scarlet colouring materials; *geranium lakes* from various eosines, phloxines, rose Bengale, &c.; *magenta lakes* from rhodamine, magenta, violets; *yellow lakes* from variously shaded yellow to orange and pure red acid colours, &c. The lakes of this group may be called *simple combined lakes.*

b. Lakes obtained by the joint or separate precipitation of colouring matters of quite different chemical nature and shades, the resulting lakes possessing other properties and quite a different shade. To this class belong *maroon lakes* from scarlets, magenta and methyl violet; *green lakes* from yellow and green, yellow and blue or violet colouring matters (olive or reseda green); the *various lakes* from scarlet, phloxine, blue, violet, &c., colouring matters, which belong to the red as well as to the (reddish) violet lakes; *leather lakes* from scarlet, brilliant or malachite green and diamond black, as also from yellow and blue colouring matters, &c. The lakes belonging to this group may be called *mixed combined lakes,* being always more or less a mixture of the shades of the colouring matters used.

a. Simple Combined Lakes

To this class belong especially the yellow, orange, bright red, blue, and violet lakes, and a few green ones (viridin lakes) of varying brightness and bluish tone.

On account of the relative small number of yellow coal tar colours known, it is impossible to manufacture a great variety of *yellow combined lakes.* Most of these colouring matters, like quinolin yellow, naphthol yellow, azo yellow, paper yellow, astacine yellow, &c., are acid colours, whilst of the basic class auramine alone is of importance for lake-making. Consequently a suitable combination of the barium chloride method with a method adapted to basic colours is the only process to be used. Auramine has a pure canary or, when strongly diluted, a lemon shade; quinolin yellow is pale lemon, naphthalene yellow a bright golden shade, azo yellow a marigold tint, while paper yellow has a brown tinge, and astacine yellow is of a greenish-olive shade. These different shades form really the whole scale of yellows, and therefore the combinations of these colouring matters are limited. The considerable brightness of the auramine lakes—auramine has a very high colouring power—and their considerable fastness to alkaline and slightly acid salts enables lighter shades to be obtained by the addition of auramine to yellow acid colours These lakes, however, are less used as true yellow lakes than for manufacturing the green combined lakes that will be described later on, because the addition of a green or blue colouring matter to the original lake increases the effect of auramine, as well as of the darker yellow acid colours.

In the manufacture of these lakes the barium lake of the acid colouring matter in question must first be made, and washed once or twice (according to its nature), the solution of auramine being afterwards added. Auramine is sometimes fixed in a small quantity by acid colouring matters without any precipitating medium, but when using larger quantities of colouring matter it must be fixed with tannin and tartar emetic, or a solution of resin and zinc salts or alum. If, as is sometimes the case, an orange or red azo colour is intended to be introduced into the lake, it must be precipitated, as a barium lake, conjointly with the yellow acid colour.

The various groups of *simple red combined lakes*—orange, scarlet, geranium lakes, vermilionettes, and lakes from the so-called insoluble pigment colouring matters—have already been described, so that all that is necessary here is to indicate how the various methods of precipitation can best be combined in practice to furnish new lakes having the most important properties belonging to both groups. Experience shows the following combinations to be of practical interest:

1. Combined precipitation of orange and red azo colours with resorcin colours, with a suitable adjustment of the carriers and quantities used in both methods. This combination produces lakes approximating in properties to geranium lakes.

2. Lakes from resorcin colours or from red azo colours or mixtures of both are combined with insoluble pigment colouring matters. This method produces a great variety of lakes with excellent properties, and therefore suitable for various purposes.

3. Vermilionettes are combined with soluble or insoluble azo colours, thus acquiring greater fastness to light and alkali, and increased brightness.

The number of *geranium lakes combined with azo colours* is at present very large, and they are nearly all made in the following way: The azo colouring matter used is first precipitated on to a suitable carrier, the lake repeatedly washed, and the solution of resorcin colour afterwards added, and precipitated by lead nitrate or lead acetate in the usual way. The colouring matter is mostly precipitated completely, the top liquor being therefore quite colourless, a result probably due to the mutual precipitation of the azo and resorcin colours. Nearly all red azo colours, from the lightest orange to the darkest scarlet, can be introduced into geranium lakes; the extensive scale of both the resorcin and azo colours enables dark brands of azo colours to be combined with yellowish resorcin colours, and conversely yellowish azo colours with dark resorcin colours, in widely varying proportions, thus producing a large number of variously shaded geranium lakes with divergent properties. These lakes have many advantages: when ground in oil they retain their full bright tone, and do not "bronze," viz., do not exhibit the metallic lustre generally observed on paintings or prints executed with pure bright geranium lakes. By careful working and the use of suitable proportions of azo and resorcin colours this defect can be entirely avoided, and suitability for calendering greatly improved. These lakes will also stand varnishing to a degree varying with the nature of the colouring matters used.

Insoluble azo colours can be combined in a similar way with resorcin colours or red soluble azo colours, or with both together. The carrier is first thoroughly mixed with the colouring matter in paste, and the soluble azo colour is afterwards precipitated on the mixture by means of barium chloride. The lake is washed and the dissolved resorcin colour is added, which, if not already fixed without any precipitant, is precipitated completely by lead nitrate or lead acetate. When basic rhodamine is used instead of a resorcin colour, complete precipitation is generally obtained by the aid of a small quantity of tannic acid and tartar emetic, sometimes with a solution of resin and a small excess of barium chloride, when soluble azo colours have been used, or with a lead salt when resorcin colours were employed. Sometimes it is more suitable to prepare the lakes repeatedly from soluble and insoluble azo colours, and to mix them afterwards in a pasty state. The resorcin colour is then precipitated on this mixed and thoroughly washed lake in the way already described. This method is generally used if the pigment colouring matter in question is decomposed or considerably changed by the influence of the barium chloride needed to precipitate the soluble azo colour. Most of the insoluble pigment colouring matters now sold darken considerably under the influence of barium chloride when precipitated jointly with soluble azo colours, and in such cases give especially dull and fugitive shades with spirit varnishes, if they have been modified by the presence of a jointly precipitated resin colour.

Almost any insoluble pigment colouring matter can be used for making the darker brands of this group of lakes when intended solely for varnish colours. The tones are modified by the aid of light or bluish scarlet and resorcin colouring matters. Light, bright spirit varnish colours, however, can be obtained from the light, insoluble pigment colouring matters, pigment orange, pigment red G, helio fast red G, &c., bluish resorcin colours (eosine 5B, erythrosine, phloxine, rose Bengale), or rhodamine. The choice of the carrier depends, of course, on the application of the lake, it being seldom that the same carrier can be used in lakes for different purposes, *e.g.*, as a painter's colour and spirit varnish pigment, since a lake which will act very well for one of these purposes is generally unfit for the other.

For *combined vermilionettes* from soluble and insoluble azo colours the remarks already passed on the subject of joint precipitation of these colouring matters will generally apply. The method is also the same, except that the choice of carriers is limited (red lead, barytes, lead sulphate, &c.). According to their use for painting, the treatment is simpler. On account of the generally bright red tone of vermilionettes, the light red pigment colouring matters, like red for lakes P, lithol red R, pigment red G, helio fast red G, helio purpurin 3BL and 5BL, even pigment red B, can alone be used, the difference in their behaviour toward yellowish and bluish resorcin colours furnishing a very extensive scale of tones. If the red pigment colouring matters are darker than those mentioned, the tones furnished with eosines will be duller, and, especially in the dry state, of a brownish cast, though less apparent when mixed with varnish.

The *magenta lakes*, now largely used for printing purposes, are combined in a variety of ways, not always suitably so with regard to fastness. The best combinations are certainly those from magenta (new magenta, rubin N, cerise, maroon, &c.) and safranine, with phloxine, rose Bengale and (reddish) violet acid colours, which not only modify the peculiar bluish tone of the magenta precipitate to an agreeable reddish tone on a white carrier, but are also quite as fast as magenta. These lakes are generally manufactured as follows: Phloxine or rose Bengale is precipitated on the carrier (alumina, artificial barytes, lead sulphate) by lead salts, or fast acid violet by barium chloride, the solution of magenta being afterwards added and precipitated by tannic acid and cream of tartar, solution of resin and zinc salt or alum, or merely by Turkey red oil. Sometimes, and especially in the last two named methods, the magenta is precipitated completely when the salts used for precipitating resorcin colours and acid violet are in sufficient excess.

The combined precipitation of violet basic coal-tar colours is restricted to the adjustment of certain relative proportions of the reddish and bluish brands of this group, the foregoing methods being used for precipitating the basic colouring matters. Combinations of basic violet colouring matters and magenta on the one hand and resorcin colours on the other, or of all three together, are occasionally sold, but cannot be recommended.

Of less value is the combination of the few brands of green acid colouring matters for the production of a series of *viridin-green lakes*, except by drawing on the basic green colouring matters (malachite and brilliant green), which, however, preclude the employment of viridin-green lakes for purposes in which they are expected to be fast to spirit.

b. Mixed Combined Lakes

In spite of the very large number of mixed combined lakes, there are really only two principal groups, viz., the *reds* and *greens*, which, when combined, produce *brown lakes* (leather lakes) and *olive-green shades* (moss green, reseda green, bronze green, &c.). The extensive scale of tones from

Dark bluish red through brown-red (maroon lakes),
Greenish-brown (bronze brown, bronze green),
Dark brownish green (olive green, moss green),
Light brownish green (leather lakes),
Light greenish yellow (reseda green),

to pure yellowish- or bluish-green lakes (viridine, light, night, may, wall-paper green) explains the great variety of possible combinations obtainable from a relatively small number of colouring matters. The predominant colours are the reds and greens, whilst the yellows, blues, and violets are used for shading purposes only. The great variety, as measured by the eye, is still further increased by the large number of the methods and their combinations, also the numerous modifications of the carriers on which the colouring matters are fixed. The attempt now made to familiarise the reader with the broad aspect of the subject must not be considered as an exhaustive treatment, but merely as an endeavour to afford a basis for independent work.

For the manufacture of all mixed combined lakes, only three initial lakes —*red, orange*, and *yellow*—can be used, these being toned by bluish-red (magenta, safranine, &c.), violet (methyl violet), blue (methylene blue, helio fast blue, &c.), green (brilliant, malachite, acid, naphthol-green, &c.), and black colouring matters (diamond black). The suitable methods of precipitation must be combined in accordance with the acid or basic nature of these colours.

The *red initial lakes* are exclusively made from red azo colours—scarlet, scarlet for lakes, brilliant scarlet, palatine scarlet, excelsior scarlet for lakes, &c.—by the barium chloride method. The yellowish brands of these colouring matters are preferably used, and, if necessary, combined with azo orange to produce certain brownish mixed lakes. Owing to the nature of red azo-colour lakes, the only way to produce mixed combined lakes containing them as an initial lake is by combining the barium chloride and the tannic acid methods. The alkaline materials (resin soap, Turkey red oil) used in the other methods of producing lakes from basic coal-tar colours would dissolve the azo-colour lake.

The most important mixed combined lakes with an initial lake from red azo colours are the already mentioned maroon lakes, and, secondly, the brown and olive-green combined lakes. *Maroon lakes* are always obtained when a lake from red azo colours is toned with magenta, safranine, or their by-products—cerise, maroon, &c. The tone is browner in proportion as a more yellowish initial lake has been used, which explains the frequent use of orange colouring matters for this purpose.

The simplest and most generally used method has been repeatedly described. The azo red lake is prepared, washed, and separated from the top liquor, the solution of magenta being then added and the colouring matter precipitated by tannic acid and tartar emetic, a corresponding quantity of methyl violet or diamond black being added if bluish tones are desired. For dark brownish shades use is made of brilliant or malachite green, with or without diamond black in addition to the magenta. By increasing the quantity of green or black colouring matters, or of both together, more brownish shades are produced, until, by omitting the magenta entirely, *pure brown lakes* (leather lakes) are obtained, *olive-green* and *bronze-green* combined lakes being produced by the aid of considerable quantities of green colouring matters.

If pure *azo orange colouring matters* are used to manufacture the initial lake, an addition of pure dark blue and dark greenish blue colouring materials, such as methylene blue, helio fast blue, &c., to the above-named red, green, violet, and black basic coal-tar colours will furnish a great variety of shades, capable of supplementing the scale of the aforesaid lakes, according to the degree of brightness and shade. In view of this possibility of producing combined lakes of these groups from colouring matters of different chemical nature, the expert must see that he selects those distinguished by special properties, such as fastness to light, spirit, and alkali.

Most of the green combined lakes formed by toning a *yellow initial lake* with green and blue basic coal-tar colours are produced in a similar manner, the shade being chiefly influenced by the varying chemical properties of the yellow colouring matters used for the initial lake, and by the different methods of precipitation. The circumstance that acid as well as basic, and even yellow colouring matters, such as flavine, Persian berries, quercitron, &c., are suitable for making the yellow initial lake necessitates a corresponding change in the method of production, besides being the cause of the different behaviour of these lakes towards the said green and basic or acid coal-tar colours (acid green, naphthol green, &c.). Hence, in making certain of these mixed combined lakes at least four quite different methods can be applied.

a. Joint precipitation of yellow and green or blue acid colouring matters by the barium chloride method.

b. Joint precipitation of yellow, green, and blue basic colouring matters by any of the methods used for these colouring matters.

c. Combination of *a* and *b*. The yellow initial lake is made from yellow acid colouring matters by the barium chloride method, and basic blue or acid green colouring matters are precipitated by tannic acid and tartar emetic.

d. Preparation of the yellow initial lake by precipitating yellow vegetable colouring matters (flavine, quercitron, Persian berries, &c.) on a white carrier by the aid of soda and aluminium salts, the basic green and blue colouring matters being then precipitated by method *c*.

The *combined viridin green lakes* are nearly exclusively made by the method *a*, as are also certain mixed lakes from yellow acid colouring matters and naphthol green, the shades of which can be easily modified in any desired way by a suitable quantity of quinolin yellow or naphthol yellow. On replacing the latter by the reddish azo yellow, the brown-tinged yellow acid colours, like pluto orange, paper yellow, or the greenish astacin yellow, various shades of olive-green lakes are produced, which are very fast to light, especially when combined with naphthol green. By addition of indigo-blue, acid colouring matters these lakes can be obtained in darker and richer shades.

The method *b* is of special importance in the manufacture of the so-called *solid greens, parrot greens,* &c., containing siliceous materials like green earth, white earth, bole, &c., as a carrier. The formation and tones ot these pigments are based on the joint absorption of auramine and brilliant or malachite green by the said carrier. Another group of partly very bright green lakes is obtained by the joint precipitation of auramine and Patent blue or of green basic coal-tar colours by resin soaps on a white carrier like barytes, artificial barytes, zinc white, china clay, &c. These lakes are, however, ot less importance, on account of their imperfect fastness.

The method *c*—viz., combination of the barium chloride and tannic acid methods—gives lakes of considerable importance, and of all shades from the brightest emerald green tint to the deepest reseda and moss green. The considerable difference between the shades is based on the variously toned initial yellow lakes as well as on the great variety of possible combinations. In fact, the initial lake can be combined with green, blue, and violet, as well as with red and brown, or even black, basic coal-tar colours, thus producing a most extensive scale of tones.

The *true green lakes* of this group are formed by covering the barium lake from quinolin yellow (see p. 491) with brilliant or malachite green, these colouring matters being precipitated almost completely by tannic acid and tartar emetic. Since quinolin yellow can also be precipitated by barium chloride in any desired proportion, we have a very favourable conjunction of circumstances for the production of very bright green lakes, suitable for various purposes. The barium lake from quinolin yellow, however, must always be washed before the solutions of green colouring matters are added, though a loss of quinolin yellow, which readily dissolves in water, be incurred. The lakes of this group to be sold in powder or lumps must be very carefully dried at a low temperature (25° to 30° C.).

If quinolin yellow be replaced by the reddish-tinged naphthol yellow, the same method will furnish a group of very suitable and popular lakes, which, though not so bright as the quinolin yellow lakes, are nevertheless satisfactory in this respect. While the lakes from quinolin yellow combined with pure blue, reddish-blue, or violet coal-tar colours, on account of the sulphur shade of quinolin yellow, are mostly dull, and therefore of not much value, the basic coal-tar colours mentioned give, combined with naphthol yellow, soft lakes of an agreeable olive-green shade. Here again the barium lake from naphthol yellow must be washed repeatedly before the solutions of basic coal-tar colours are added. The resulting combined lakes must also be carefully dried at a low temperature.

According as the aforesaid yellow acid colours are replaced by more reddish, brownish, or greenish colours, like azo yellow, pluto orange, paper yellow, astacin yellow, &c., and if the resulting barium lakes are used alone or combined with green, blue, reddish-blue, or violet colour bases, a number of differently coloured lakes can be obtained. In most cases the precipitation of the basic colours can be effected by tartar emetic and tannin.

Though the green combined lakes obtained from yellow coal-tar colours are now largely used, they have only partly displaced the older *lakes from yellow vegetable colouring matters,* the latter exhibiting a peculiar warmth of tone which cannot be imitated by coal-tar colours. Chief among these vegetable colouring matters are flavine, Persian berries, and in certain cases quercitron (extract), the fixation of which on the carrier—alumina, artificial barytes, barytes, china clay, whiting, &c.—is effected by a single method, based on the capacity of alumina to fix these vegetable colouring matters completely. In practice a hot solution of aluminium sulphate or alum is treated with a hot solution of soda containing the dissolved colouring matter, so long as a precipitate of aluminium hydroxide is formed. The colouring matter is nearly always precipitated completely when equivalent quantities of alum (or aluminium sulphate) and soda are taken, the yellow vegetable colouring matter in this case acting as an indicator. In point of form and purity flavine is the more suitable material, being sold in the dry state (as a fine powder), completely soluble in any desired proportion of soda solution. It is therefore more easily applied than Persian berries or the usually thick fluid extract of quercitron, and, apart from its greater purity and colouring power, it produces much brighter and purer toned yellow lakes. Consequently it is the only vegetable colouring matter now used for making pure toned green lakes, though the price is rather high. Persian berries and quercitron are exclusively used in the manufacture of certain yellow lakes (the Schütt yellow of the Germans) of a peculiar shade, which cannot be obtained by the aid of flavine.

In order to produce this yellow pigment, the Persian berries are repeatedly extracted with a hot or boiling solution of soda; the extracts are collected, and precipitated on barytes, gypsum, china clay, &c., by the aid of a solution of aluminium sulphate or alum, with constant stirring. Provided the liquor from the precipitate is kept absolutely neutral, the fixation of the colouring matter is generally complete. In the reaction of the aluminium salts with soda a dense viscous scum is produced, which retards the work. These yellow lakes are also very difficult to wash, because the fine precipitate of alumina settles down very slowly, and therefore easily separates from the quickly deposited carrier. This defect can be easily observed, especially in the washing in the filter press, and for this reason these yellow lakes are mostly left unwashed.

The simpler quercitron lakes are generally made by the same method. Here the extract of Persian berries is replaced by a solution of soda and quercitron extract, the same carrier being used. Better qualities of lakes from quercitron, particularly those used for wall- and fancy papers, are made by boiling about 160 parts of quercitron extract (32° B.) with 10 per cent. of castor oil and a fivefold quantity of water for a certain time. Aluminium sulphate (one-fifth of the weight of the quercitron extract, in a tenfold quantity of water) and one-sixteenth of tin salt are then added, the whole being afterwards precipitated by a solution of soda (about one-sixth of the weight of extract), with continued stirring. The lake is afterwards boiled again for some time, and washed two or three times. Such lakes have a good covering power and are very bright.

To manufacture green lakes preference is given to those from flavine and quercitron (more rarely the above-named yellow lakes from coal-tar colours), the former (as already mentioned) in making pure green shades, the latter for olive greens. The method is the same as already described. To obtain pure green lakes the washed flavine lake is treated with a solution of green basic coal-tar colour—preferably brilliant or malachite green—and afterwards precipitated by tannic acid and tartar emetic. Most vegetable colouring matters have the property of fixing a certain quantity of basic coal-tar colour, especially brilliant and malachite green. Though this fact is partly due to the tannic acid content of the vegetable colouring matters, such precipitations are not so fast as the true tannic acid ones, and therefore the green colouring matter is always completely precipitated by adding tannic acid.

The pure green flavine lakes are largely used for wall- and fancy papers, or as so-called non-poisonous greens for toys, and are sold both in paste and as a powder. In the former state they always contain artificial barytes as a carrier, cheaper kinds containing certain quantities of fat white clays or gypsum, both of which yield bright lakes. The powdered lakes chiefly contain barytes, gypsum, sometimes calc spar, as a carrier, the defective covering power of which is improved by an addition of white clay. Green flavine lakes are easily manufactured; they are not liable to any change during the various processes, the tones are always uniform, the lakes settle down easily, filter quickly, and dry well at high or low temperatures. They are easily ground, except when containing an excessive quantity of fat clay.

On account of the decided reddish-yellow tone of quercitron lakes, they can seldom be used for manufacturing pure green shades, being always of a more olive green in comparison with flavine lakes. This can be observed the more clearly the closer the shade of the green colouring matter used for the initial lake approximates to blue; and a true olive is obtained when greens are replaced by pure blue colouring matters for combining with the yellow initial lake. The so-called *true leather lakes* are obtained in this way by combining the lake from quercitron with light blue colouring matters like patent blue, alkali blue, &c.; or *reseda-*, *olive-*, or *moss-green lakes* by means of dark blues, like Victoria blue, helio fast blue, methylene blue, &c.

The various intermediate shades between these two groups are formed by suitable additions of methyl violet, magenta, Manchester brown (vesuvine), and even brilliant black. Quercitron lake is often mixed with logwood lakes (blacks as well as the so-called bronze lakes), to obtain a very dark combined lake, and is afterwards toned with green, blue, or red-violet basic coal-tar colours. In this case the colouring matter used for shading is rarely precipitated by tannic acid or other precipitating agents, the quantity being small as a rule, and completely fixed by the quercitron lake.

The combination of these yellow lakes from Persian berries or quercitron with the basic colours mentioned is effected in exactly the same way as described; but these are seldom found on the market. Owing to their relatively low intensity, these yellow lakes are far from being bright, and are sometimes far inferior in other respects to the foregoing combined lakes. Combined lakes obtained from quercitron or Persian berries lake, however, are very fast to light, which is more than can be said of those from other yellow vegetable colouring matters or coal-tar colours.

5. Lakes from Adjective Colours

The most important representative of this group of colours is *alizarine red* (the natural colouring matter of madder root), the artificial production of which has been already mentioned on p. 476. Besides this colouring matter, *alizarine orange, alizarine brown, alizarine Bordeaux, alizarine yellow, alizarine blue, acid alizarine blue, cœruleine,* and *galleine* are used for making lakes, but only to a small extent in comparison with the true alizarine red.

All the above adjective colours can be worked up into lakes, which, on account of their very good properties—especially the nearly absolute fastness to light—play a considerable part among the lake pigments from vegetable or coal-tar colouring matters.

However much the various methods known or recommended for precipitating the adjective colours may vary in detail, the precipitation really consists in the conversion of the colouring matter (dissolved as an alkali salt) into an insoluble and characteristically coloured combination of the metal oxide used as a precipitating medium and the acid of the colouring matter. This precipitating agent is always aluminium oxide, and is taken into combination in its purest form from alum, by the acid of the colouring matter used.

Though the manufacture of alizarine lakes from madder is nearly out of use and of only historical interest, a short description will be given for the sake of completeness.

The raw material almost exclusively used in the manufacture of *madder lakes* during the second half of the last century was *garancine*, a by-product said to have been first prepared by *Colin* and *Robiquet* by treating ground madder with strong sulphuric acid. It formed a mixture of charred woody fibre and the whole of the colouring principle present in the madder, isolated by the sulphuric acid. The manufacture of garancine, which was partly a commercial industry and partly practised by colour-makers themselves, was based on the fact that the colouring matter of madder is not decomposed by sulphuric acid, and therefore by charring the woody fibre enveloping the colouring principle this latter can be isolated and transformed into a suitable condition. The ground madder was first put into water containing 0·5 to 0·75 per cent. of sulphuric acid, in order to remove sugar, gum, and soluble organic derivatives, and to decompose any calcium salt present. It was then filtered, and washed till the washings no longer exhibited a yellow colour. The purified madder was next partly dried by heavy pressure, and afterwards treated in lead-lined boxes with its own weight of sulphuric acid (66° B.), which completely charred the woody fibre in a few days, the mass looking like charcoal. To remove the sulphuric acid this madder charcoal was washed in tanks provided with a filtering arrangement until the washings were no longer acid. The residue on the filter constituted garancine, which, if properly made, contained twice as much colouring matter as the same weight of ground madder.

For conversion into alizarine lakes, madder charcoal was then treated with about eighty volumes of water in wooden tanks, about three-eighths of its weight of iron-free alum being added, and the mixture boiled by steam for several hours. After a certain time the charcoal settled to the bottom, the hot top liquor was passed through a flannel filter, and the residue in the tank was again treated with the same quantities of water and alum. This process was repeated several times, the rest of the charcoal on the filter being always united with the residue in the tank. The orange-red filtrates were allowed to cool, separately or together, whereupon the colouring matter partly precipitated in soft, ochreous yellow flakes, which were collected by filtration and used for manufacturing the finest brands of madder lakes, while the filtrates were used exclusively in making the less bright pink lakes.

The colouring principle of madder contained in the alum solution was afterwards combined with alumina by converting the alum into that form. According as the precipitation was effected with soda, potash, ammonia, tin salts, whiting, &c., so the colour and strength of the madder lakes varied. Generally the precipitation of the alum was not quite complete, but only carried so far that the filtrates from the lakes were slightly tinged with red, in order to avoid an excess of alkali, which would lower the brightness of the colour. This, too, also explains why the older brands of madder lakes were mostly hard, and occasionally had a vitreous fracture.

Since the discovery of synthetical alizarine this and similar methods of manufacturing alizarine lakes have lost their importance, and are now rarely practised, even the most distrustful customers being now convinced of the good properties of lakes from artificial alizarine.*

The methods used at present for manufacturing alizarine lakes not only differ very considerably from the older ones, but in consequence of their superiority furnish lakes of such brightness and intensity as would have seemed incredible a few years ago. The numerous recipes seem to differ very slightly, though some are very carefully guarded trade secrets, and therefore cannot be given here.

As already mentioned, the production of madder lakes relies on a combination of the acid of the colouring matter with alumina, precipitated simultaneously with the colouring matter in the form of aluminium hydroxide from a solution of alum by an alkali carbonate. In the reaction the quantity of aluminium hydroxide is always much greater than is necessary to fix the acid, and the surplus therefore serves as a base. The precipitation is always effected in the cold; the formation of the lake is therefore very imperfect at first, but as the temperature is raised to boiling the formation and the intensity of the lake increase. Since the combination follows the precipitation, and only at boiling heat, the method is therefore an operation intermediate between precipitation and dyeing.

In addition to the salts necessary to produce aluminium hydroxide, other materials, like Turkey red oil, sodium phosphate, calcium salts, &c., are generally used, their effect being, however, only partly explained by the formation of the lake, though it is certain that in their absence the resulting lakes are far less bright and intense. Whilst the part played by Turkey red oil in this process as a brightening medium can be explained by its similar behaviour in Turkey red dyeing, the effect of phosphoric acid still remains obscure, all that is known being that it forms an integral portion of the lake, and that in its absence the lake suffers in brightness. The same applies, but in a still higher degree, with regard to the effect of the calcium salts, the presence of which in the lakes not only improves the brightness, but is also necessary in the case of certain colouring matters of this group if a favourable product is to be obtained.

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* In some countries—France, &c.—a few true madder lakes are still manufactured on a small scale as finest artist's colours, and are said to be brighter, especially in oil. As a matter of fact, sometimes alizarine lakes of very great brightness are found on the market, which, ground in oil, are considerably less bright than certain duller-looking kinds. [TRANSLATOR.]

A most important point in the process is to keep the solution as weak as possible in order to secure brilliancy and fineness of structure in the coal-tar colour lakes. In view of the great sensitiveness of alizarine toward iron, all iron articles, like nails, pipes, &c., that might come in contact with the precipitation mixture must be carefully excluded and replaced by lead or tin.

The best proportions for dissolving are the following:

1. Colouring matter .	1 : 20	using the following proportions of each	350 parts by volume.
2. Sodium phosphate .	1 : 20		750 " "
3. Calcined soda .	1 : 20		200 " "
4. Turkey red oil, 50 %	1 : 10		100 " "
5. Alum . . .	1 : 20		250 " "
6. Lime-water .	1 : 30		25 " "

The cold solutions of soda and colouring matters are first united in the precipitation tank, and the stirrers are set going immediately, the sodium phosphate and Turkey red oil solutions being added afterwards. When a sufficiently intimate mixture of these solutions has been obtained the solution of alum is slowly added in small portions to prevent excessive liberation of carbonic acid gas. A certain time afterwards—depending on the more or less complete escape of the carbonic acid—the lime-water is added, and the mixture is continually stirred for at least ten to twelve hours. If this cannot be done during the night-time it must be continued next day, and the precipitation mixture is afterwards—in this latter case the third day—heated for at least six to eight hours. The heating process requires especial care and attention. As a rule, the only way to produce specially bright and pure red alizarine lakes is by very gradual heating for a certain time, the longer the better. The steam is admitted in such a manner that actual boiling of the whole mass does not begin for four or five hours, and then this condition is maintained, with continual stirring, for two or three hours, until no further improvement in brightness can be discerned. The steam is then turned off, but stirring is continued for some hours, the finished lake being washed repeatedly, filtered, and dried, preferably at ordinary temperatures.

Experience shows that the brightest and most handsome tints in Turkey red dyeing are only obtained by steaming under pressure (in the "hot flue"). Based on this principle, a number of recipes for producing the brightest tints of alizarine lakes have been introduced, and in some large colour works alizarine lakes of great intensity and brightness are now produced by such methods, one of which is reproduced below.

Solution I.—22 lbs. of 20 per cent. alizarine are mixed with 5½ galls. of water, and added to a solution of 4 lbs. of calcined soda in 4 galls. of water. The mixture is then heated, with continual stirring, to about 50° C. in an hour. A cold solution of 19¼ lbs. of sodium sulphate with 19¼ galls. of water and 8¾ lbs. of Turkey red oil (50 per cent.) are afterwards added.

Solution II.—11¾ lbs. of aluminium sulphate (free from iron) are dissolved in 11 galls. of water, and thoroughly mixed with a solution of 5½ lbs. of calcium acetate in 5½ galls. of water. Solution I. is then added to Solution II., and the whole afterwards heated for an hour in an autoclave without pressure, the mass being subsequently heated about three hours under a pressure of 4 to 5 atmospheres, thoroughly well washed, filtered, and dried at the ordinary temperature.

To apply this method to that just described the resulting lake is boiled for one hour by steam, filtered, and brought, unwashed, into the autoclave, where t is boiled for two to three hours under a pressure of 4 to 5 atmospheres.

By the same method the other adjective colours can be worked up into more or less suitable and very fast lakes. These colouring matters are: *alizarine orange, alizarine brown, alizarine maroon, alizarine yellow, alizarine blue* anthracene blue, alizarine indigo blue, &c.), *acid alizarine blue, alizarine green, galleine, galloflavine* in paste, *alizarine black, cærulein*, &c.

With alizarine orange, alizarine blue, alizarine indigo blue, and alizarine green a slight modification must occasionally be introduced, since these colouring matters cannot be dissolved in soda solution, but must be mixed with a fivefold quantity of water, stirred up with the solution of aluminium sulphate or alum, and precipitated by the mixture of solutions of soda, sodium phosphate, and Turkey red oil. That is to say, the method described on p. 520 is reversed, all the other manipulations remaining the same.

A special method is published (by the *Badische Anilin- und Soda-fabrik*) for the preparation of lakes from *cærulein*:

22 lbs. of cærulein are mixed with 27½ galls. of water, 44 lbs. of sodium bisulphite (38° to 40° B.) are added, and the mixture allowed to stand at the ordinary temperature for twelve hours. A further 27½ galls. of water are added, and the whole heated by steam to 70° C., filtered, and the clear liquor diluted with 110 galls. of water. The liquor is then raised to boiling, 44 lbs. of potassium alum are added, and the whole boiled for half an hour without any interruption. 33 lbs. of sodium bisulphite (38° to 40° B.) are then added, and boiling repeated for half an hour. The precipitated lake is filtered, washed, and dried at the ordinary temperature.

In all these methods the base is produced at the same time as the lake. f properly worked they produce lakes of uniform intensity, brightness, and other physical properties, and are therefore among the best known in colour-making, though complex and occupying a long time. Slight changes n the weights of the raw materials and small additions of shading agents ike iron and tin salts will furnish very bright, fast lakes by any of the described methods. The same applies to a suitable combination of the various colouring materials. These lakes will be very suitable for various purposes, especially for artist's colours, printing inks, &c.

Azarin red may also be mentioned here, though chemically it belongs to the azo colours. It is precipitated by the same method as alizarine colouring matters, and is therefore generally classed along with the adjective colours. The *Höchst Farbwerke, late Meister Lucius und Brüning*, the only makers of this colouring matter, give the following instructions:

	Lake A (dark).			Lake B (light).
Water	250	parts	by volume	—
Sodium phosphate, 1 : 10	—			175
Solution of soda (calcined), 1 : 10	70	,,	,,	60
Turkey red oil, 1 : 10	20	,,	,,	50
Sodium stannate, 1 : 10	20	,,	,,	20
Precipitate, with a mixture of				
Azarin S, 1 : 10	70	,,	,,	10
Alum solution, 1 : 10	500	,,	,,	500

In the manufacture of *azarin lakes* the various operations, temperature, time, &c., are the same as described in the manufacture of alizarine lakes on p. 520. To obtain brilliant red or pink shades, the materials used, water, and plant must be absolutely free from iron, since the least trace of that metal would considerably dull the shade of the produced lakes.

6. Insoluble Azo and Diazo Colours and their Use in Manufacturing Lake Pigments

The first attempts at producing insoluble azo colouring matters direct on the fibre was made by *R. Holliday* at Huddersfield and *Fr. Graessler* at Cannstadt, but their methods were too difficult to use in practice. *Horace Köchlin* (the well-known Alsatian chemist) showed at the Paris Exhibition (1889) a series of azo colouring matters directly produced on the fibre by his own process, kept secret. Shortly afterwards the *Höchst Farbwerke* published a method, distinguished by great simplicity and absolute safety, which quickly found application for cloth dyeing and printing.

The Höchst process is still used to-day in practically the same form, but has been extended to include a whole series of shades, from primrose through red, Bordeaux, and blue to the deepest black, a pure green being the only member of the colour scale lacking.*

The possibility of producing this large number of azo colours direct on the fibre without any technical difficulty led to the idea of discovering a similar method for manufacturing lakes. The original difficulties—the insufficient plant in small or medium colour works, the scarcity of ice, especially in summer-time, &c.—have now mostly been overcome, partly by simplifying the process (for instance, manufacture of azophor red,† viz., diazotised paranitraniline), and partly by improving the plant. The process, which has been extended to a considerable number of azo colours, is now the common property of most well-equipped colour works, so that nearly the whole series of this class of colouring matters are met with in the trade under the generic name of "ice colours," &c.

The *insoluble azo colours* are the so-called naphthol-azo colouring matters, obtained by treating aromatic amines or diamines with naphthol. The products obtained by the aid of *betanaphthol* are of a specially high value for the manufacture of lake pigments distinguished by special fastness to water and light, great brightness, and simplicity of manufacture. The production of the colouring matter is based on the coupling of the diazo derivatives obtained from amines with betanaphthol. Success depends on the right order of the various operations, the neutralising of the diazo hydrochloride derivative and the surplus hydrochloric acid used for diazotisation by an alkali. The production of bright shades depends primarily on the perfect conjunction, which in turn depends on the maintenance of distinct conditions during the reaction of the two components.

The first operation in the manufacture of insoluble azo colours is the conversion of betanaphthol into the soluble form, ***sodium naphthol*** being the most suitable. To obtain this body the weighed quantity of betanaphthol is mixed with hot water to a fairly thick mass, a corresponding quantity of caustic soda is added, and heated (if necessary) until the whole of the naphthol is dissolved. The purity of the caustic soda plays a certain part, because if contaminated with sulphate it produces shades deficient in brightness. For various reasons the quantity of caustic soda in the naphthol solution is considerably higher than necessary to produce sodium naphthol, especially in dark azo colours. The more alkaline the solution of naphthol the higher the permissible acidity of the solution of diazo derivative. On the other hand, an excess of caustic soda increases the brightness of the shade; but this must not be pushed to excess, many azo colours having a tendency to "bronze" in such a case. The solution of sodium naphthol slowly turns brown under the influence of air and light, and will give brownish products, on which account it must always be freshly prepared, or, at any rate, kept in closed bottles.

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* The manufacture of these pigments has made a great advance during the last few years. The idea of some that the insoluble azo colours in addition to the so-called pigment colouring matters (p. 496) will be completely substituted for the old-fashioned artificial mineral colours must, however, be considered an absurdity. [TRANSLATOR.]

† Höchst Farbwerke, late Meister Lucius und Brüning.

The second operation, requiring more care and attention, is the production of the diazo solution, the so-called *diazotisation*.

The diazo or tetrazo derivatives from amines and diamines are formed by treating hydrochlorides or sulphates of these aromatic amido derivatives with free nitrous acid. As a rule they are readily decomposable bodies, and for this reason their formation is dependent on definite conditions, the most important of which, according to the information published by the *Höchst Farbwerke, late Meister Lucius und Brüning*, are as follows:

1. *Excess of Acid.*—Most aromatic amines are very easily diazotised in presence of a certain excess of acid. At the same time the presence of free mineral acid prevents or retards the formation of decomposition products from the diazo solution (diazo-amido derivatives, phenols, &c.). In practice the excess of acid is about 20 to 50 per cent., more rarely 75 to 100 per cent., above the quantity necessary to form the salts of the amines and to decompose the nitrite.

2. *Excess of Nitrite.*—Here again an excess favours the diazotisation by replacing the loss of nitrous acid caused by the stirring. The excess of nitrite, however, should not be more than 10 per cent., for economical reasons, as well as on account of the injurious character of the large quantity of vapours to the workmen.

In large works the nitrite to be used for diazotising purposes is generally kept in stock solution. Before preparing the solution it is advisable to determine by titration with potassium permanganate, by the method described on p. 323, the precise amount of sodium nitrite in the stock solution.

3. *Temperature.*—The most favourable temperature for producing diazo derivatives is that of melting ice, and therefore most amines must be diazotised at a temperature of about 0° C., but not higher than 5° C. A considerable rise in the temperature of the liquids can always be observed in diazotisation, and a suitable excess of ice must therefore be used, to preclude any detrimental effect of this heat on the reaction. The concentration of the solutions has, however, considerable influence on the progress of the diazotising process; the stronger the solutions to be diazotised the greater the thermal reaction, and the larger the quantity of ice necessary to counteract the results. Conversely, very dilute solutions can be used for

diazotisation without ice, a fact which proves very useful in practice. Such low temperatures, however, are not required for all amines, certain of the aromatic amines being diazotisable at ordinary temperatures, or even in a lukewarm state.

Nitraniline, nitrotoluidine, naphthylamines, benzidine, tolidine, dianisidine, diphenetidine, chloranisidine, azo black base, &c., are diazotised cold, whilst amidoazobenzene, amidoazotoluene and nitrophenetidine (blue-red O) are treated at 20° to 30° C.

Owing to the large quantities of ice required in the manufacture of these diazo compounds, the colour-makers endeavoured to find products containing diazo derivatives in a stable form. Examples of these latter are the *azophor colours* (Höchst), *azophor red* and *azophor orange*, which deserve attention on account of the greater ease and simplification of the diazotising process.

4. *Fine Distribution of the Amido Bases or their Salts.*—The hydrochlorides or sulphates of the amines to be diazotised being very sparingly soluble in presence of an excess of acid, the free nitrous acid has often to react on the finely crystallised salts, in which case their complete solution as diazo derivatives ensues only when they are present in a micro-crystalline form. On the other hand, crystals of a certain size are not acted upon by nitrous acid. Hence it is of the greatest importance that the amines, in the state of salts or free bases, should be used in an extremely finely divided form: (1) The amido base is first converted into a very finely divided hydrochloride or sulphate, which is afterwards treated by the nitrite solution; or (2) a so-called *nitrite paste* is prepared from the amido base and the nitrite solution, and this mixture is afterwards treated with dilute hydrochloric or sulphuric acid.

Before dealing with the manufacture of the insoluble azo colours used for manufacturing lakes we may give the most important facts relating to the naphthols and amido bases used for that purpose.

a. Naphthols

Of the two known naphthols, betanaphthol is by far the more important. The colours it produces are not only far brighter, but also much faster to light and water, whereas the insoluble naphtholazo colours from alphanaphthol are generally darker, of a dull shade, and partly less fast to light. Hence alphanaphthol is rarely used in colour manufacture, or only for shading purposes.

Betanaphthol is sold in lumps as well as in fine powder. The latter is, of course, easier to use, since it dissolves much quicker than the lumps when treated with hot water and caustic soda.

Though commercial betanaphthol is generally pure, it is necessary in all cases to test it accurately, so as to ensure uniform products. The perfect solubility of betanaphthol in alcohol is a sufficient criterion, since any impurities or adulterations insoluble in alcohol—*e.g.*, common salt, sulphate, dextrin, &c.—are thereby readily detected. Betanaphthol must, in addition, be free from alphanaphthol, a very small fraction indeed being quite sufficient to dull the colour, especially in the case of the very important paranitraniline red.

Besides betanaphthol, certain other naphthol preparations are used, the most important of which is betanaphthol R, used for producing very blue-tinged brands of paranitraniline red.

b. Amido Bases

The chief amido bases now used in practice include paranitraniline, nitrotoluidine, benzidine, tolidine, dianisidine, and alphanaphthylamine. Besides these bodies, amidobenzene, producing a very bluish-red, and amidoazotoluene, giving very bright maroon tones, may be mentioned, though the lakes obtained from amidobenzene are much less fast to light than paranitraniline red.

Paranitraniline.—The following commercial brands are obtainable :

Paranitraniline, yellowish .	to yellowish-red colours.
„ extra . .	to bluish-red colours.
„ extra, bluish .	to obtain the brightest and most bluish-red colours.

All these brands are sold as a finely ground powder, fine crystals, or as 25 per cent. nitrite paste, already containing the quantity of nitrite necessary for diazotising. These various brands may be considered chemically pure, paranitraniline being now obtained free from isomeric bodies. Ground paranitraniline powder being very voluminous and tending to repel water, on account of the interstitial air, the fine crystalline form is preferable, as being easier to work and dissolve. The powder is preferred when the user desires to prepare the nitrite paste himself.

In the manufacture of lakes the nitrite paste is rarely used, the fine crystalline powder being exclusively employed, the solution of which (as hydrochloride, more rarely as sulphate) is treated with the solution of nitrite in the cold. The conversion into hydrochlorides or sulphates, which, as already mentioned, must be produced in a very finely divided state, is effected by dissolving the weighed quantity of paranitraniline in boiling water, with addition of acid, 1 molecule of paranitraniline requiring 2·2 to 2·5 molecules of hydrochloric acid or 1·1 to 1·25 molecules of sulphuric acid for complete conversion. If the solution is afterwards slowly cooled by continued stirring, the salt generally falls down as such minute crystals that complete diazotisation easily takes place on the addition of ice and the nitrite solution.

Attempts have been made to work without ice, but this can only be done by using a considerable excess of acid and very dilute solutions. Since, however, it may be occasionally necessary to resort to this somewhat cumbrous method, the proper quantities of materials to be used may be now given.

1·4 kgs. of powdered paranitraniline extra are thoroughly well mixed with 3 litres of hot water, 2·8 litres of hydrochloric acid (22° B.) being afterwards added, and stirred for a quarter of an hour. Next 12·5 litres of very cold water are poured in, followed at once by 1·6 litres of nitrite solution (290 grms. per 1 litre), with continued stirring, until the whole is diazotised. The quantity of water may, of course, be increased. Before use the diazo solution must be made up to at least 100 litres by adding cold water.

Nitrotoluidine is sold as a brownish-yellow powder or as a 25 per cent. nitrite paste. It produces a bright orange with betanaphthol, and is also very similar to paranitraniline.

Nitrophenetidine (blue-red O) serves to produce bright pink or bluish-red tints which are also fairly fast. Blue-red O (Höchst) is 25 per cent. orthonitroparaphenetidine, and is diazotised, without ice, at about 15° to 20° C. The diazotisation is complete if the prepared nitrite paste contains a suitable excess of nitrite, and the resulting diazo derivatives are very fast.

Amidoazobenzene gives with betanaphthol very bluish, full, and fairly fast reds. It is best diazotised at 15° C.—*i.e.*, without ice.

Amidoazotoluene is sold as a base and as 100 per cent. hydrochloride. The diazo derivatives produce a bright, fast maroon with betanaphthol. Amidoazotoluene can be diazotised without ice at 15° C.

Alphanaphthylamine is sold as "alphanaphthylamine salt S" (Höchst) in the form of a very fine white powder, very sparingly soluble in water. When mixed with water, ice, and hydrochloric or sulphuric acid it is easily diazotised on the addition of a sufficient quantity of nitrite solution, and produces dark, fairly fast Bordeaux-red shades with betanaphthol. Fineness of division is essential, and for this reason alphanaphthylamine is sometimes sold as hydrochloride in paste, which, however, is rarely used. The diazotisation process is the same as already described. The hydrochloride exhibits certain defects, the paste easily drying into a coarsely crystalline state during transport and storage, and darkening considerably under the influence of light and air, in which state it is diazotised with difficulty and leaves a certain amount of residue.

Benzidine (benzidine base, benzidine sulphate) is used for producing brown shades by the aid of betanaphthol. On partly replacing betanaphthol by alphanaphthol the shade can be darkened in any desired way. The brown colour is fairly fast to light. Benzidine is of only small importance for manufacturing lakes.

Tolidine is very similar to benzidine, but the brown shade obtained with betanaphthol has a more violet tinge, and is somewhat faster to light.

Azophor colours (azophor red PN and azophor orange MN) (Höchst). Azophor red is the stable form of the diazo derivative from paranitraniline. It forms a yellowish, very light powder, and is fairly soluble in water, a small residue (0·5 to 1 per cent.) being left. It is hygroscopic, and must therefore be kept dry in not too warm a place, protected from direct light.

According to the makers' instructions, azophor red is best dissolved in a tank provided with a tap close to the bottom. The tank being partly filled with water, the weighed quantity of azophor red is added, well stirred, and the tank filled up with water. After stirring a certain time the mass is allowed to stand, whereupon the light, voluminous scum rises to the surface of the liquor, and the latter can be drawn off, except for a small remainder, which is afterwards clarified by washing and passing it through a woollen filter.

The Manufacture of the Insoluble Azo Colours

The process is one that is applicable to all amido derivatives, and consists of three principal operations, viz.:

1. Preparing the alkaline solution of betanaphthol.
2. Preparation of the diazo solution—*i.e.*, diazotisation of the amido base.
3. Coupling (combining) the two solutions.

For these operations two tanks, holding about 220 and 750 galls., are necessary, the smaller being placed above the other in such a manner that its contents can flow into the latter. Both tanks should be provided with stirrers. The smaller tank is for preparing the diazo solution, the larger one for dissolving the betanaphthol and for receiving the carrier. From what has already been said it follows that the insoluble azo colours will be the brighter the greater the dilution of the solutions. Hence the tanks should be as large as possible.

The above dimensions will therefore not be suitable for all cases, but are sufficient to deal with the quantities mentioned in the following examples.

1. Preparing the Betanaphthol Solution

This can be done direct in the larger working tank. For this purpose the tank is filled with about 44 galls. of water, and 16½ lbs. of betanaphthol, mixed with water to a suitable paste, are afterwards added through a sieve to secure uniform distribution. The stirrers are set to work, and as soon as the naphthol is sufficiently disseminated through the liquid 3¼ galls. of caustic soda (20·5° B.) are slowly added. Stirring is continued till all the betanaphthol is dissolved, the operation being accelerated by warming the liquid to about 40° to 45° C. by direct steam.

The betanaphthol being completely dissolved, the carrier (barytes, artificial barytes, alumina, &c.) is generally added at once in the usual form of a thin pulp run in through a fine sieve. The volume of the liquid is afterwards made up to 200 galls., and if the coupling process has to be effected at a temperature below 5° C. ice is added until the prescribed temperature is obtained.

2. Preparation of the Diazo Solution

The amido bases are diazotised in the colour works in varying serial order, so far as the several operations are concerned, the main object being to minimise the loss of nitrous acid. This result is, however, very seldom achieved, the acid being able to escape even when the utmost precaution is observed in working.

The most important factors of easy diazotisation having already been mentioned, we have now only to deal with the practical performance of the various stages.

The smaller tank is first supplied with about 650 galls. of cold water, and the stirrers are set to work. In an open barrel 15½ lbs. of ground paranitraniline extra are treated with 13¼ galls. of boiling water, well stirred, 2¼ galls. of hydrochloric acid (22° B.) being added to the mixture. When, after having been stirred for a certain time, all is dissolved the liquid is allowed to cool slowly, in order to obtain the paranitraniline in the finest possible form, which done, the liquid is ladled into the diazotising tank. A sufficient quantity of ice (about 1 cwt.) is then added, and the whole is stirred until the temperature does not exceed 5° C. This temperature being the most favourable for diazotising, the nitrite solution is added at once, of course with continued stirring. The above quantity of paranitraniline requires 3 galls. of nitrite solution (a slight excess), containing 29 per cent. of nitrite (8¼ lbs. in all). The operation must be assisted by thorough stirring, the liquid being then made up to 110 galls. by adding cold water (and more ice if necessary), and the diazo solution used immediately for coupling the betanaphthol in the lower working tank.

The tap near the bottom of the diazotising tank being opened, the diazo solution is slowly run as a thin stream into the solution of naphthol, which is kept stirred. The insoluble azo colour is immediately produced from the sodium salt of betanaphthol and the diazo derivative; but, notwithstanding the quickness of the coupling, a difference can be observed in the behaviour of the various diazo derivatives. The rapidity of the coupling, for instance, also depends largely on the nature of the diazo solution, paranitrodiazobenzene, for example, being coupled far more quickly than its product azophor red. These facts, which we cannot stop to explain here, sometimes necessitate stirring the liquor for several hours even after the coupling process. On the other hand, much finer division of the azo colour is obtained by this manipulation (but the solutions must not be rendered too concentrated by it), as also a thoroughly equal coloration of the base, properties of the greatest influence on the brightness and uniformity of tone.

The lake pigment is then washed two or three times in the precipitating tank, filtered, pressed, and dried in the usual way.

To obtain the same lake from *patent azophor red PN* the method is considerably simplified, as already explained in the description of this product.

16½ lbs. of betanaphthol require about 62 lbs. of azophor red, which are dissolved in 55 galls. of water. The solution is afterwards made up to 110 galls., and subsequently treated like any other diazo solution, cooling with ice being, however, superfluous.

The *Badische Anilin- und Soda-fabrik*, of Ludwigshafen, has also published the following method for working without ice :

30¼ lbs. of paranitraniline are mixed to a uniform paste with 2¼ galls. of cold water and 16½ lbs. of sodium nitrite by the aid of a wooden stick, which operation requires great care, since unmoistened particles are not diazotised. 11 galls. of cold water are added to the paste, and the mixture passed through a sieve into the diazotising vessel. It is afterwards diluted with 55 galls. of cold water, and 88 lbs (=7¾ galls.) of hydrochloric acid of 20° B. strength (or 74 lbs. = 6½ galls. of 22° B. strength) are then added at once. After stirring for a quarter of an hour the diazo solution is ready. A slight turbidity is harmless, and the diazo solution need not be filtered.

For the naphthol solution 33 lbs. of betanaphthol are dissolved in 11 galls. of boiling water and 28½ lbs. of caustic soda (40° B.). 22 galls. of cold water are afterwards added, followed by 22 lbs. of calcined soda dissolved in 22 galls. of water.

The carrier (for instance, 8 cwt. of barytes) is mixed with the naphthol solution, and the diazo solution is slowly added, with continual stirring. A yellowish-red lake is obtained, which is washed twice.

To obtain a bluish-red lake, naphthol R is used to form the naphthol solution, and 2 cwt. of Turkey red oil F are added afterwards. It is advisable to add a solution of 11 lbs. of aluminium sulphate in 11 galls. of water after the lake is precipitated.

The foregoing weights, as well as the instructions and manipulations to be used for diazotising and finishing, are the same in the case of the other amido derivatives.

Coal-tar Colouring Matters Used for Manufacturing Lakes (1907)

The following list is an alphabetical arrangement of the coal-tar colouring matters specially used for manufacturing lakes. The colouring matters marked * give especially good lakes. The letters in the parentheses ( ) after the name of the colour indicate the maker.

[According to a special communication from Geo. Zerr, one of the authors, the colouring matters marked † produce *lakes very fast to light.*—Translator.]

*Acid alizarine blue BB (H.)
* „ blue B, R, G (S.)
* „ green L (B.)
* „ „ extra conc. B (Cas.)
* „ „ conc. D (H.)
„ magenta G (H.)
* „ violet 4R, 6BN (Bad.)
* „ „ 6B (G.)
* „ „ 3RA, N (H.)
*Alkali blue 4B (L.)
* „ „ 6, 7, R, 2BH (H.)
* „ „ 3B (173F) (W.)
* „ „ 6B conc. (D.)
* „ „ 6B extra, 6B, 5R (Bad.)
„ „ f. printing ink (Bad.)
„ violet 6B (Bad.)
*†Alizarine orange N (H.)
*† „ red 2A bluish blue, 1B new (H.)
*† „ „ RX, SDG, 5F (H.)
*† „ „ PS, powd. IB extra, 20 per cent. paste (B.)
† „ „ V20, bluish (Bad.)
*Alphanaphthylamine salt (H.)
*Amaranth red B (Cas.)
Amido azotoluene, 100 per cent. (H.)
Anthracene yellow GG, BN (Cas.)
Anthraquinone violet (Bad.)
*†Astacine red B (Bad.)
*Auramine O, II (B.)
* „ OE (Bad.)
* „ G, OI (I. B.) (with green earth†)
* „ O (G.)
* „ O (J.)
* „ O (H.)
*Autol orange (Bad.)
* „ red GL.† BGL, BL.† RLP, RLV bluish (paste) (Bad.)
*Azarine S (H.)
Azetopurpurin 8B (A. B.)
Azine green TO, T (L.)
Azo acid yellow (A. B.)
„ carmine B (Bad.)
„ red RLP (Bad.)
„ rubin SG (A. B.)
* „ yellow O (H.)
* „ „ 33525 (W.)
Azoflavin SL (Bad.)
Azofloxine 2G (B.)
*Betanaphthol (Cas.)
* „ R (H.)
*Betanaphthylamine base (Bad.)
Biebrich scarlet (K.)
„ acid blue (K.)
*Bismarck brown F (B.)
Blue green S (Bad.)
„ red O (H.)
*Bordeaux double conc. G (A. L.)
„ „ „ G, R*, O (H.)
Brilliant azurine B, 5G (B.)
„ benzo blue 6B (B.)
* „ black B (Bad.)
* „ carmine L (Bad.)
„ cresyl blue 2B (L.)
* „ croceine 3B, 3B conc., 20722 (B.)
* „ „ M, MOO, B, BOO, 9B (Cas.)
* „ „ 292 (D.)
* „ „ B, 5B, BB, R, yellowish (H.)
„ diazine blue B, BB, BR (K.)
„ double scarlet 3R (B.)
* „ green cryst. extra (H.) (with green earth †)
* „ orange G, R (H.)
* „ red R, G (f. lakes) (Bad.)
* „ rhoduline red B (B.)

*Brilliant scarlet G, R (Cas.)
* " sky blue (I. B.)
* " violet 5BO (Basle)
*Bromofluoresceine AL (H.)
Capri blue GON (B.)
* " " GON, GN (L.) (with green earth †)
China yellow B (Cas.)
*Chinolin yellow (Quinolin yellow) (A. B.)
* " " " " (Bad.)
Chloramine brown G (B.)
" orange G (B.)
" yellow M, GG (B.)
*Chloranisidine P (Bad.)
Chromazone red AA, AN (G.)
Chromotrope 2R, 6B, 10B (H.)
Chrysoidine EN, crystals, cryst. R (Cas.)
" A (Bad.)
" O (L.)
†Citronine G, A (L.)
Cloth red O (H.)
Congo orange G (B.)
Cotton light blue O, soluble in water (H.)
*Cotton scarlet extra (Bad.)
Cresyl fast violet 2B (L.)
*Croceine 292 (D.)
* " scarlet 10B (B.)
*Crystal scarlet 6R (H.)
* " violet (Bad.)
*Curcumein ff., GG (A. L.)
Cyananthrol RB, R, RA (Bad.)
Cyanol FF (Cas.)
Dark blue 25868 (W.)
Diazine black (K.)
Direct yellow R extra (B.)
" " extra conc. (Basle.)
Eosamine B (A. B.)
*Eosine O extra, 4J, OO extra (L.)
* " CPhl (T.)
* " 35 (33531), 23 (33530), B, 2G 5G (W.)
* " B extra (A. B.)
* " A5G, A2G, BB, 5B (H.)
* " A, LA, LG, J, BNL, W extra (Bad.)
* " GGF, 6G (Cas.)
* " extra yellowish S, extra bluish S (B.)
* " acid L new (Bad.)
Erythrine C (Cas.)
" X f. lakes (Bad.)
*Erythrosine (H.)
* " G (Bad.)
* " B yellow (Cas.)
*Excelsior scarlet f. lakes, JN, JJN (Cas.)
†Fast navy blue R (Oehler)
†Fast orange O (H.)
Flavindulin (Bad.)
*Formyl violet S4B (Cas.)
Galleine A (H.)
*Gold orange extra conc. (D.)
*Green PL (Bad.)
*Guinea green G, 12157, B, B extra (A. B.)
*Guinea violet 4B (A. B.)
Helio azurin RL, BL (B.)
*† " fast blue BL, SL (B.)
*† " fast red G (paste) (B.)
* " orange RM (B.)
" purpurin B, 3BL*, 4BL, 5BL*, 10BL* (B.)
Helvetia blue (G.)
Indanthrene in paste (Bad.)
Induline scarlet (Bad.)
Isorubin (A. B.)
*Lake blue I (Bad.)
* " " CB (Cas.)
* " " RT (A. L.)
*† " Bordeaux B (A. B.)
" green BW (Cas.)
* " orange ON (Bad.)
* " red 4614, A101 (A. B.) †
* " " 78, 413 (D.)
* " " P†, C (H.)
* " scarlet LE, GH, GC, RC, 2RZ, 3RN (Bad.)
* " " LN, LGN (Bad.)
* " " GG, R (Cas.)
* " " G extra, L, B extra (L.)
* " violet R (A. B.)
*†Lithol red R, GG paste (Bad.)
*Malachite green cryst. (A. B.) (with green earth †)
Malachite green cryst. (H.) (with green earth †)
*Manchester brown EE (Cas.)
Madarin G extra (A. B.)
Marine blue BN (Bad.)
Metanile yellow extra (A. B.)
" " PL (Bad.)
" " 43F (W.)
Methylene blue BG, BH (Bad.) (with green earth †)
* " " BB, BB conc., 22890 (B.)
* " " BBO, BB (Basle)
* " " BB (Cas.)
* " " B extra conc. (G.)
* " " R, BB (H.) (with green earth †)
* " " 2B (K.)
" green extra yellow conc. (H.)
" violet RRA, BN (H.)
*Methyl green SF (K.)
* " violet MB extra, BB extra, 3B extra, *B extra (Bad.)
* " " 5B, B (B.)
* " " 2B (H.)
Mikado yellow G, 6G (L.)
" gold yellow 4G, 2G, 6G, 8(
" orange 3RO, 4R (L.)
*Milling yellow O (Cas.)
*Mordant yellow R, G (Bad.)
†Naphthol R (Bad.)
*† " yellow S (B.)
*† " " S (Bad.)
*† " " S (H.)
*† " " S extra conc., 3363 (W.)

*†Naphthol green B (B.)
*Neptune green S, SB, SG, SBN (Bad.)
New bengaline 74R, A, 74 (K.)
* „ magenta (B.)
* „ „ O (H.)
„ metamine blue M (L.)
* „ methylene blue F, FR† (B.)
* „ „ „ GG (Cas.)
„ patent blue GA (B.)
* „ red L (K.)
* „ solid green BB (Basle.)
* „ Victoria blue (B.)
Night green A extra, 32P (W.)
Nigrosine W, C (Bad.)
*Nile blue BB, R (Bad.)
*Nitrosamine red (Bad.)
*Nitrotoluidine C (Cas.)
*Opal blue, greenish (H.)
*Orange IIB (B.)
* „ II, ME, SP, MR (Bad.)
* „ ENL, extra*, II* (Cas.)
* „ E (K.)
* „ G extra, 3837, A (L.)
„ A (L.)
* „ RR, 2L (H.)
* „ T8359, II, II conc. 522/F (W.)
Oxydamine red S (Cas.)
Oxamine violet, pat. (Bad.)
*Palatine lake scarlet GG, G (Bad.)
*Paper yellow 3G, A (Bad.)
* „ „ GG extra (B.)
*Paranitraniline extra bluish (H.)
* „ S (B.)
*Patent blue L, A (H.)
Peri wool blue BG, G (Cas.)
*†Permanent red 6B paste (A. B.)
*Phosphine RRR, GG extra (A. B.)
* „ GG extra (H.)
Phloxine BB, *BA extra 0, BA extra, GA extra 0 (H.)
* „ BBN, G (Bad.)
*Pigment Bordeaux R, N paste (H.)
* „ chlorine GG (H.)
*† „ chrome yellow L paste (H.)
„ fast yellow R, G (H.)
*† „ orange R (H.)
* „ purple A (H.)
*† „ red B, G (H.)
*† „ scarlet 3B (H.)
*Pluto orange G (B.)
*Powder magenta AB, dark, A (Bad.)
Primuline A (Bad.)
„ (Cas.)
*Pyramine yellow G, G f. lakes (Bad.)
*Pure blue O (H.)
Quinolin—*see* Chinolin
*Rhodamine B extra, S, G, 6G (B.)
* „ B extra, 6G (Bad.)
* „ B extra, G extra (I. B.)
* „ B extra, *extra B (H.)
Rhoduline heliotrope B (B.)
* „ red G (B.)
„ violet (B.)
Rose Bengale (A. B.)
* „ „ NTO, NT (Bad.)
*Rubin N (A. B.)
„ W (H.)
*Safranine T extra, MN (Bad.)
* „ BS, S150 (Cas.)
* „ extra bluish (K.)
* „ RRA (H.)
*Scarlet GRL (A. B.)
* „ for silk (Bad.)
* „ 4GB, RRL, BO extra, 6RB, 58940 (A. B.)
* „ GRLC, 3RL, 4R (A. B.)
* „ GVL, 57299 RL, 4BGL, 44099 (A. B.)
* „ GL, RL, 57298, 3RB (A. B.)
* „ 2RL (B.)
* „ G f. lakes, R, RR f. lakes, BN (Bad.)
* „ FR, EC (Cas.)
* „ GG, 2R (J.)
* „ 2RX (A. L.)
* „ GR, GRL, 2RL, 5R, 3RL,† GRLH (H.)
* „ V, RL, RLV, GR (H.)
* „ R, 26474 (W.)
Sky blue (I. B.)
*Solid green FII (I. B.)
Sulfone yellow R conc. (B.)
Tannin heliotrope (Cas.)
Tartrazine (Basle)
*Thioflavin T (Cas.)
*Turquoise blue G, GL extra, BB (B.)
Uranine (A. B.)
Vermilion scarlet R, G (A. L.)
*Vesuvine BL (Bad.)
* „ 4BG, conc. (H.)
*Victoria blue R, B, 4R (Basle)
* „ „ B (Bad.)
* „ yellow conc. (H.)
* „ pure blue B (Bad.)
Violet BB 55 (W.)
*Water blue R (H.)
„ „ 3R (166A3/F) (W.)
Wool blue BB, R, 5B (A. B.)
* „ „ N extra (B.)
*Xylene blue AS (S.)
*Xylidine scarlet R (A. L.)
Yellow green I, II, III (Bad.)

Abbreviations

A. B.—Actiengesellschaft f. Anilinfabrikation, Berlin.
A. L.—Leipziger Anilinfabrik vorm. Beyer u. Kegel, Leipzig.
B.—Bayer u. Co., Leverkusen-on-Rhine.
Bad.—Badische Anilin- u. Soda-fabrik, Ludwigshafen-on-Rhine.
Basle.—Basler Chemische Fabrik, Basle.

Cas.—L. Cassella u. Co., Frankfort-on-Main.
D.—Dahl u. Co., Barmen.
G.—J. R. Geigy u. Co., Basle.
H.—Farbwerke vorm. Meister Lucius u. Brüning, Höchst-on-Rhine.
I. B.—Ges. f. Chem. Industrie, Basle.
J.—C. Jäger, Düsseldorf.
K.—Kalle u. Co., Biebrich-on-Rhine.
L.—Farbwerk Mühlheim vorm. Leon[illegible] u. Co., Mühlheim-on-Rhine.
S.—Chemische Fabrik vorm. Sandoz, Basle.
W.—Chem. Fabrik vorm. Weiler-ter-Meer, Uerdingen-on-Rhine.

[Owing to the great advance in lake-pigment making, already mentioned on pp. 450 and 467,
Indigo (Bad.), (H.), and the class of
Sulfine colours, the most important of which are

Pyrol green (L.), Katigen green (B.), Katigen olive (B.)
Pyrol blue (L.), Katigen indigo (B.), immedial blue (Cas.)
Pyrol yellow (L.)
Pyrol brown (L.), Katigen brown (B.),

can also be used for manufacturing lake pigments.—TRANSLATOR.]

ANALYSIS OF LAKE PIGMENTS: PRODUCING LAKES IN THE LABORATORY

The methods of testing for coal-tar colouring matters on the fibre as well as in the form of lakes are very incomplete, inasmuch as the colouring matters do not all give equally favourable results, no simple characteristic reactions capable of sharply differentiating the individual members of a group of colouring matters having yet been elaborated. The methods published by *E. Weingärtner* in the *Bulletin de la Société de Chimie de Mulhouse* (December 1886) and the *Chemiker-Zeitung* (1887, Nos. 10 and 12) enable the most important groups of colouring matters and their individual members to be recognised in their original form; but, generally, incorrect results are obtained when the same colouring matters occur as insoluble lakes. This fact is due partly to the change of character on precipitation, partly to the presence of a variety of colouring matters in the same lake, the reactions of the individual being consequently masked. Even if the nature of the colouring matter were not changed by the precipitating medium to such an extent as to render the tests inoperative, the manner in which the insoluble lakes to be analysed have to be dissolved must surely modify the chemical nature of the colouring matter. The presence of the solvent—strong sulphuric acid, alkalies, &c.—must disturb the typical reactions, if they do not entirely destroy them. Another difficulty is the exceedingly large number of colouring matters now used in the manufacture of lakes, which, while very similar chemically, often vary considerably in shade and other chief properties.

Systematic testing after the manner of the qualitative analysis of inorganic bodies is consequently still unknown in the chemistry of coal-tar colours,* and will probably never be established in such a complete form. The analyst is therefore restricted to certain chemical reactions and typical indications shared by the best-known coal-tar colours and their lakes—indications which, as already mentioned, do not always settle the identification of a colouring matter, but permit fairly reliable conclusions to be formed with regard to the group to which the colouring matter in question belongs.

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* A remarkable advance in the analysis of lake pigments may be referred to here. It is given in the recent work *Bestimmung von Teerfarbstoffen in Farblacken*, by Geo. Zerr, 1907 (Dresden, Steinkopf u. Springer), an authorised English edition of which will soon be published. [TRANSLATOR.]

When the analyst, from the appearance of certain reactions, believes that a particular group of colouring matters is present in a sample of lake which has to be matched, all that he can generally do is to check the accuracy of his opinion by making corresponding tests on the individual members of the group of colouring matters in question.

In modern colour works laboratory precipitations play an analytical part, inasmuch as, besides fixing the shade of a sample to be matched, they are also intended to detect the colouring matter which imparts the special properties of the lake in question. This work is sometimes very difficult, and requires great patience and perseverance.

In the analysis of lakes from coal-tar colours generally, certain physical properties or the method of application may greatly assist in the classification of the colouring matter sought for. For instance, the fact that a certain lake will stand varnish generally shows that it does not contain colouring matters soluble in alcohol, a conclusion that shuts out whole groups—for instance, the basic colouring matters, nearly all the members of which are dissolved by alcohol. The same applies to the degree of fastness to acids and alkalies. The characteristic colour of the lake under examination, its fastness to light, the softness, the specific gravity, and other properties, too, often allow a reliable conclusion to be formed as to composition and colouring principle. The experienced analyst is able to distinguish a red alizarine lake, for instance, from an eosine lake immediately, or a pure viridin green lake from a lake obtained by mixing; nor has he any difficulty in detecting with the naked eye, for instance, the often very slight difference between a lake from croceine or scarlet and the true scarlet lakes.

When, however, simple or mixed combined lakes containing three or more colouring matters are to be tested, the skill acquired by many years' experience and exercise is less reliable. In such cases a true analysis must be made by means of all the reactions available. There are but few reactions which are applicable to and give reliable results with all the coal tar colouring matters used for lakes—viz., the behaviour of the lake

(*a*) Towards alcohol;
(*b*) „ acids, especially strong sulphuric acid;
(*c*) „ caustic soda;
(*d*) „ the reducing property of a solution of hydrochloric acid and tin salt.

The following table explains the reactions of the chief coal-tar colours with the chemicals named. It must, however, be mentioned that the specified colour change produced with some lakes, as well as their solubility in alcohol, may undergo considerable modification in precipitation or by the special nature of the carrier used. For example, the barium chloride lake from pigment scarlet 3B (Höchst) is totally insoluble in alcohol, whilst the tin lake is fairly soluble in absolute alcohol.

REACTIONS OF THE MOST IMPORTANT LAKES FROM ARTIFICIAL COLOURING MATTERS

Abbreviations: d., decolorised; D., decomposed; s., solution.

The Lake is coloured with	C_2H_5OH.	HCl.	H_2SO_4.	NaOH.	$SnCl_2$ + HCl.
Magenta	Extracts, gives bluish-red s.	Yellow	Yellow	Brown at first, afterwards almost d.	d.
Safranine	Extracts, s. rubin-red fluorescence	Conc.: blue s.; dilute: red-blue s.	Black tint, changing to green	Red s.	When heated, d.
Acid magenta	Extracts slightly	No change	Like HCl	Brown tone	d.
Purpurin	Red s.	On boiling: yellow s., lake becomes yellow	„	Lake and s. red	Pale yellow s.
Eosine	Pink s., strong greenish fluorescence	Wine yellow	Pale yellow	D. when heated; s., strong fluorescence	Lake turns orange, the liquor pale yellow
Erythrosine	Red s., less fluorescence	Yellow-brown precipitate	Yellow	Red s., or like eosine. but less strong	Like eosine
Phloxine	Extracts slightly	Yellow	„	Red s.	—
Rose Bengale	No effect or slightly blue-red col. s.	„	„	„	—
Aurine	Extracts colouring matter	„	„	„	—
Alizarine	No effect	Strong: lake yellow; liquid, wine yellow	D.; on addition of NaOH, red-violet	Violet	Orange yellow; liquor: pale yellow
Orange II	Orange-yellow s.	Bluish-red s.	Raspberry shade s.	Brown-red s.	d.
Scarlet G and R	Slight yellow s.	Brown-red s.	Like HCl, somewhat more bluish	Red-brown s.	Partly d.
Croceine scarlet	Little effect	Violet, later on greenish blue	Blue	Bluish	d.

„ 3R	—	**Unchanged or slight effect**	Unchanged or bluish-red s.	„	—
„ 5R	**Extracts the colouring matter slightly**	**Slight effect or red s.**	Scarlet s.	„	—
„ 6R	Slightly coloured	Slight effect or slightly blue-red s.	Red-blue s.; by transmit. light: red-violet	Scarlet to brown-red s.	Sometimes lighter coloured
Lake red P (Höchst)	Effect slight	—	Handsome deep red-violet	Blue-violet–red-violet	—
„ C (Höchst)	„	—	„	—	—
Lithol red R (Badische)	„	—	Bright blue-carmine	—	—
„ GG (Badische)	„	—	Reddish-carmine s.	—	—
Pigment red B (Höchst)	„	—	Bluish red-violet	Dark blue-red violet, the lake deepens in colour	—
„ „ G (Höchst)	Dissolves a little	—	Magenta-like s.	—	—
„ orange R (Höchst)	„ „	—	Carmine s.	—	—
„ purple A (Höchst)	„ „	—	Bluish-magenta s.	—	—
„ scarlet 3B (Höchst)	—	—	Light yellow scarlet-like s.	Brown-red	Light red to orange
Cloth red O (Höchst)	Pale raspberry s.	—	Dark blue, turning to red	—	—
Amaranth B (Cassella)	Insoluble	—	Dark blue, turning to green	—	—
Fast red BN (Badische)	„	—	Dark blue, turning slightly reddish	—	—
Autol red RLP (Badische)	Scarlet s.	—	Dark blue, turning to red	—	—
Pigment Bordeaux N, R (Höchst)	„	—	„	—	—
Helio fast red G (Bayer)	Slightly soluble	—	Paris blue shade	—	—
„ purpurin 10BL (Bayer)	—	—	Indigo shade	Colour remains, slightly yellow s.	—
„ „ 4BL	—	—	Carmine s.	Brown-red s.	—
„ „ 5BL (Bayer)	—	—	Dark blue-carmine	Red s.	—
„ „ 3BL (Bayer)	Sparingly soluble	—	Yellowish carmine	Yellow-red s.	—
Lake red 4644 (Berlin)	—	—	Red-violet: diluted with water: brown-red	—	—

REACTIONS OF THE MOST IMPORTANT LAKES FROM ARTIFICIAL COLOURING MATTERS—*continued*

The Lake is coloured with	C_2H_5OH.	HCl.	H_2SO_4.	NaOH.	$SnCl_2 + HCl$.
Brilliant carmine L (Badische)	Insoluble	—	Bright carmine	Brown-red, colouring matter slightly dissolved	—
Bordeaux R (Höchst)	—	Small effect, liquor brown-red	First violet, afterwards blue	Yellowish-red s.	Pale violet
Picric acid	Yellow s.	Colouring matter is extracted on boiling; liquor: greenish yellow	d.	Orange-red, s. yellow	d.
Naphthol yellow S	,,	d.	d.	Lake becomes paler	Like NaOH
Chrysoidine	,,	Red	Yellow	Bleached	d.
Fast yellow	Slightly soluble, yellow	,,	Lake brown-red, s. red	Brownish-yellow s.	First pale red, then d. afterwards
Auramine O	—	d.	d.	d.	—
Quinolin yellow	—	—	—	—	—
Phosphine	Slightly soluble	Yellowish s.	Greenish-yellow s.	Bleached	Partly d.
Malachite green	Green s., turning to blue	Light orange	Deep orange	d.	d.
Brilliant green	Green s.	,,	,,	,,	,,
Acid green	Faint green s.	Lake turns paler	Lake turns brown, liquor yellow	,,	Lake turns yellow
Cœruleine	—	Lake darkens; liquor: red	Lake darkens; liquor: wine-yellow, dull	,,	—
Alizarine blue	Absol. C_2H_5OH: faint red-violet s.	Lake violet: s.: yellow red	Conc.: violet s.; dilute: lake violet, liquor pale red	Bluish-green s.	Lake first violet, turning bluish red when warmed; liquor brown
Rosaniline blue	—	Blue s.	Red-brown	Reddish brown	Blue s.
Alkali blue	Blue s.	Lake greenish blue, s. green	,,	Firstly red, then d.	—
Methylene blue	Greenish-blue s.	Bluish-green liquor	Green	Bluish violet	d.
Methyl violet	Violet s.	Wine-yellow s.	Like HCl	Lake firstly bluish, then d.	Blue s.
Bismarck brown	S. red or pink	Red	Dark red	—	—

In using the table it should be remembered that the reactions mentioned for combined lakes containing two or more variously shaded acid coal-tar colours may be masked by the different behaviour of the components, and therefore rendered inexact. This disadvantage is less noticeable when combined lakes from acid and basic coal-tar colours are present, since the latter are mostly soluble in alcohol, and the remaining acid lake can afterwards be treated with sulphuric acid or caustic soda. Hence for this kind of lakes the results given in the table are fairly reliable.

The analysis of a lake pigment, so far as concerns the detection of the colouring matter by the aid of the foregoing table, is performed in the following manner:

1. Treatment with Alcohol

A small portion of the lake in question is sprinkled with absolute alcohol in a test-tube, and the mixture is slightly warmed for some time. If a coloured solution is formed, it is filtered from the residue, and the clear liquid is examined by transmitted and reflected light. According to the strength and colour of the alcoholic solution, and the presence or otherwise of a greenish, bluish, or reddish fluorescence, especially by reflected light, a preliminary conclusion can be formed with regard to the colouring matter in question. The alcoholic extraction is repeated until complete—*i.e.*, as long as the alcohol becomes coloured—the extracts being then united and the alcohol carefully evaporated. The residue of isolated colouring matter is dissolved in water and examined further. Sometimes the alcoholic solution should be diluted with half its own volume of distilled water, and the mixture heated until the alcohol is completely expelled, leaving the colouring matter dissolved in the water, or in the solid form if insoluble in the latter.

2. Treatment with Strong Sulphuric or Hydrochloric Acid

When the alcoholic extract leaves a perfectly colourless residue, this latter is tested by the usual methods of analysis.

A coloured residue from the alcoholic extraction, or—when the colouring matter is totally insoluble in alcohol—the pure lake, is treated with strong sulphuric acid, and heated, if necessary, until the lake is entirely decomposed. This operation, besides modifying the colour, usually effects the decomposition of some of the ingredients of the carrier, such as alumina, starch, &c., and artificial or ordinary barytes (when present) is partly dissolved by the concentrated sulphuric acid. A change of the colouring matter from red or orange into carmine red, Bordeaux red, raspberry, Paris blue, indigo blue, green, or yellow, or from blue into red, orange, yellow, grey, or black, or finally from green into yellow, orange, brown, &c., gives a fairly good indication as to the nature of the colouring matter in question.

After the change of colour has been carefully observed the sulphuric acid solution is poured into a beaker containing a suitably large quantity of distilled water, and examined to see whether the colour

(*a*) Resumes at once its original shade ;
(*b*) Disappears partly or entirely ;

(*c*) Resumes its original or assumes another colour after prolonged standing;

(*d*) The original tint in (*a*) and (*c*) is restored direct or after passing through various other shades.

All these characteristic signs may be exhibited by the various groups of colouring matters or by their individual members; and, in conjunction with the reactions described above, will enable an accurate conclusion to be drawn as to the class to which the colouring matter belongs, so that there will be little difficulty in tracing its commercial name.

The following reaction, which is sometimes also given by the corresponding lakes, is decisive in the case of many (especially basic) colouring matters. It consists in the faculty of many coal-tar colours of changing back, after being decomposed by sulphuric acid and neutralised by alkali, either into the original shade or into another more characteristic one. The reaction is more definite when the solution in strong sulphuric acid is carefully neutralised with caustic soda, the mixture being cooled and shaken for some time with a large quantity of ether. After standing a while the ether forms a characteristically coloured zone on the surface of the liquid. This test should always be applied in addition to the others mentioned, since it enables, for instance, magenta to be clearly distinguished from safranines, and certain basic violet and green colouring matters from similarly toned acid colouring matters.

3. Treatment with Caustic Soda

Another sample of the lake to be tested is warmed with 20 per cent. caustic soda, which generally decomposes the lake completely. In this case also certain of the carrier ingredients, especially alumina, are dissolved, whilst others, such as barytes, gypsum, artificial barytes, lead sulphate, clay, red lead, &c., are unchanged. The treatment of the lake with caustic soda is of slight importance with regard to the identification of the lake, since few of the coal-tar colours resist the influence of caustic soda so as to afford any especial characteristic indications, most of them being completely decolorised or destroyed. It is only in the case of a few vegetable and coal-tar colours that anything like the original or a similar colour is restored by neutralisation with dilute acids.

Most colouring matters which have to be developed on the fibre, and some of the new pigment colouring matters, are not decomposed by caustic soda when certain conditions are observed. Red for lakes P in paste (Höchst) is coloured a bluish red by caustic soda.

Nevertheless, the practised analyst, by observing the changes produced by caustic soda in conjunction with the results of the alcoholic and acid tests, will be able to draw many valuable conclusions, and therefore the soda test—apart from its value in identifying the carrier—should never be omitted.

4. Treatment with a Solution of Tin Salt and Hydrochloric Acid

What has already been said with regard to the reaction with caustic soda is more or less applicable to the reaction of lake pigments with tin salt and

REACTIONS OF THE MOST IMPORTANT VEGETABLE AND ANIMAL COLOURING MATTERS WITH ACIDS, ALKALIES, AND ALCOHOL

Abbreviations : s., solution ; p., precipitate ; d., discoloured.

Name.	Soluble in H_2O.	HCl or H_2SO_4.	Alkalies.	Alumina Salts (Alum, Alumina, &c.).	Bleaching Powder Solution.	C_2H_5OH.
Campeachy wood (extract)	Brown-red s.	Red s. and p.	Reddish violet	Blue-violet p.	Red-brown p.	No effect
Catechu (cutch)	Yellow-brown s.	Becomes lighter or yellow p.	Brown orange to red brown	—	Brown or yellow-brown p., or d.	—
Chlorophyll	—	—	—	Green p.	d.	Green s.
Cochineal	Yellowish-red s.	Red	Purple red to violet	$Al_2(OH)_6$=carmine	d.	No effect
Turmeric	Nearly insoluble	Red brown	Red brown	—	—	Orange s., greenish fluorescence
Fustet (extract)	Reddish-yellow s.	Turns paler	Less reddish	$Al_2(OH)_6$=orange red	Brown p.; boiled: d.	No effect
Fustic (extract)	Yellow s.	Turns paler, yellow p.	Reddish yellow	$Al_2(OH)_6$=yellow	Brownish yellow, then d.	—
Persian berries (extract)	Brownish-yellow s.	Yellow-brown flaky p.	Orange	$Al_2(OH)_6$= brownish yellow	Dark red-yellow, d., grey p.	—
Gamboge	Yellowish emulsion	Yellow p.	Red	$Al_2(OH)_6$=reddish yellow	d.	Red s.
Indigo	—	—	—	—	Brown	Boiled: blue s., soon d.
Indigo carmine	Blue s.	—	Greenish blue	—	d.	—
Purree (Indian yellow)	—	Gas liberated turns paler	Darkens	—	Ultimately d.	—
Carmine	—	Turns yellow, pure dissolved	NH_3 : violet s.	—	..	—
Madder	Slightly soluble, then slightly red	Turns yellower	Blue red	Reddish-yellow s. or p.	,,	—
Lac-dye	—	Yellow s.	Red-violet s.	—	d.	—
Litmus	Blue-violet s.	Red	Blue	Red p.	Turns paler, then d.	—
Lo-kao	—	Red	—	—	d.	—
Annatto	—	Pale yellow s.	Orange s.	Orange p.	Quickly d.	Light yellow s.
Orchil (extract)	Yellow s.	d.	Yellow red	Soon d.	Immediately d.	Bluish-red s.
Persio (red indigo)	Red-violet s.	Red	Violet	Red	Ultimately d.	—
Purple (French)	—	Turns paler	,,	—	d.	—
Quercitron (extract)	Yellow s.	Yellow-brown p.	Turns paler	Yellow p.	d.	—
Redwood (extract)	Yellow-orange s.	Yellow red	Carmine	Red s.	Yellow or orange	Pale yellow s.
Santal wood	Slightly soluble	—	Violet	Red p.	d.	Blood-red s.
Safflower carmine	—	Yellow-brown p.	Yellow	—	d.	Red s.
Woad	Greenish-yellow s.	Turns darker	Golden	—	d.	—

hydrochloric acid, most lakes being hereby temporarily or permanently discoloured. The reaction, however, sometimes affords reliable indications of the nature of the colouring matter under examination. The test is applied in the same manner as that with caustic soda.

It has already been explained that the above methods will rarely identify all the colouring matters in a combined lake, except in a few very simple kinds. Generally the colouring matter used in making the initial lake can alone be detected, whilst those used for shading—a knowledge of which is very important in matching the lake—can rarely be identified, especially when a mixture is in question. Even if such were possible, however, the proper examination of a sample is often rendered difficult or impossible by other circumstances. For instance, the sample supplied is frequently too small—*e.g.*, a scrap of paper with a little of the colour printed on it. In such cases additional means have to be employed, the best of these being comparison with a large collection of standard types, the examination being extended to other properties as well as appearance, viz., fastness to light, alkalies, and acids, covering power, softness of grain, resistance to high temperature, behaviour under varnish, &c.

The *standard types* also play an important part in checking the results of analysis. By their aid it is possible to repeat the characteristic reactions of the colours to which the results of the analysis seem to point as being present. Such a collection of standard types can be prepared by the usual methods of 10 per cent. and 20 per cent. precipitations of the chief coal-tar colours mostly used for lake-making on a white carrier (generally barytes). When the analyst is of opinion that a sample is compounded of certain colouring matters, he mixes the corresponding standard types first without regard to the shade, and tests this mixture by the same reactions as were applied to the sample.

The analysis of the carrier is a comparatively easy matter, and can be performed whilst testing for the colouring matter by incinerating a dry or ground sample of the lake. In most cases a white residue is obtained, the relative solubility of which when treated with hydrochloric acid affords an insight into its composition, the soluble and insoluble portions then being analysed as usual. In correlating the results it should be remembered that the components of the carrier were not necessarily introduced in a finished state, but may be secondary products. Barium sulphate, for instance, is often formed by the precipitation of a colouring matter with barium chloride in a solution containing aluminium sulphate. Experience will indicate which combinations are likely to exist.

The second part of the task, the synthetical imitation of the sample, can now be attempted, the first point being to determine the most suitable combination of methods for precipitating the various colouring matters in question, which done, the requisite modification of the quantities of the colouring matters and precipitants in order to obtain the desired shade and brightness may be proceeded with.

In these laboratory trials the same rules must be followed as already laid down fully on p. 338.

On account of the great variety of the lakes, their preparation in the laboratory requires far more care than in the case of matching mineral colours. It will seldom be possible to reproduce the results afterwards in the works if the notes on the process are confined to particulars of the quantities and perhaps temperature of the solutions of the salts and colouring matters used. The nature of the raw materials plays an important part—their purity, content of active substance, moisture, &c.; in a word, a number of facts which are very often insufficiently considered, especially by those who have had no chemical training. It often happens that lake pigments manufactured on the basis of laboratory experiments differ from their prototypes in brightness, and generally this fault is attributed to errors in weighing out the colouring matters. Should the same result occur (perhaps in a greater degree) with the next batch, the weighing of which has been carefully checked, the manufacturer is often puzzled, and in such event generally ascribes it to a "laboratory error," which he then tries to correct by adding more colouring matter, thus increasing the cost. The real cause of the trouble is, however, generally the different raw materials used in the laboratory and the works respectively. Certain salts and colouring matters when kept in the laboratory will get dry, whilst others absorb water from the air, thereby undergoing considerable alteration, so that the formulæ elaborated with much care and trouble in the laboratory either give quite different results, or must be entirely changed. It is therefore advisable to change the laboratory stock whenever a fresh supply of raw materials is laid in, or else to repeat the laboratory experiments with the raw materials in stock at the works on a somewhat larger scale before the lake is actually manufactured.

This precaution is the more advisable in the case of pasty raw materials, like artificial barytes, alumina, lead sulphate, &c., the moisture content of which has not been recently determined. If the percentage of dry matter be ascertained before the colour is manufactured in the works, and the quantities readjusted accordingly, much time and trouble may be saved.

The laboratory work can also be considerably simplified if successful samples (whether they match the pattern or not) be kept for subsequent occasions. For this purpose, of course, the experiments must be numbered serially, so that when a similar pattern comes up again the experiment in question may be referred to. Samples of this kind often prevent great waste of time, owing to the possibility of identifying a colouring principle in a pattern of unknown composition by the comparative reactions of previous samples. In the same way a fairly correct idea can be obtained of the various physical properties of the lake (covering power, fineness, fastness, brightness, &c.) and the approximate composition of the carrier.

The notes made of the laboratory work cannot be too ample. Besides the quantities of water, temperature, results, &c., the exact names and makes of the colouring matters used should be always fully stated, as well as any characteristic indications, such as changes of tone according to the working temperature, and changes produced by storage, drying, &c.

The yield of lake must always be noted exactly, since this being of the highest importance in *calculating* the cost price, any error may result in serious pecuniary loss. Laboratory calculations, however, are always merely approximative, the true criterion being the yield obtained in the works. This may differ considerably from the laboratory result, for various reasons; for instance, the loss of colour adhering to the filter cloths, sieves, mortars, &c., is considerably higher in the laboratory than in the works. Consequently, except for errors in manufacture, a higher yield is always obtained in working on a large scale.

Whereas, with reasonable care, there is little risk of serious error in calculating dry lake pigments, the lakes in paste require constant checking. The variations in the water content, especially when smaller than allowed for in calculating, may result in very serious errors. Here again, therefore, the laboratory results must not be relied on, but each batch on issuing from the press must be carefully tested for the percentage of water present.

The calculation of cost prices plays a most important part in the preparation of lakes in the laboratory, for it may easily happen that when a sample has been matched at great trouble the calculation process shows it to be too dear, and in this case, of course, further laboratory work must be repeated until a cheap enough product is obtained. A thorough knowledge of the prices of the raw materials is therefore an essential preliminary to facilitating work in the laboratory, and the practice of some manufacturers of keeping their technical assistants in ignorance of these prices, from the fear that they might get to learn too much about the business, is one that merely results in injury to their own interests.

INDUSTRIES

E.—THE USES OF COLOURS

The manufactured colours are chiefly used in two different ways: either they are incorporated with a vehicle and spread over the surface of the article to be coloured ("painting"), or they are introduced—alone or in association with other substances—into the mass of the body to be coloured, and in some cases chemically combined therewith ("dyeing").

Painting may be divided into two classes: ordinary (painters and decorators) and artistic painting. According to the method of treating the pigments, the printing industries and the fancy paper branch may also be grouped with this class. Animal or vegetable fabrics, wood, leather, paper, &c., are "dyed." In painting, the finely divided dry pigment is applied in a liquid vehicle; in dyeing, the colouring matter is introduced in a state of solution or suspension into the body to be dyed, or else is developed in or upon it.

In painting and similar applications almost any kind of colours can be used, though some are better adapted for certain purposes than others. In painting, however, the vehicle is of special importance, and greatly influences the effect and durability of the colour; in fact, the vehicle is the predominant factor, for any given colour will not work equally well with all vehicles.

Colours may also be applied without any vehicle at all—for instance, writing or drawing with lead pencil, the colouring principle of which is very finely divided plumbago, or with a colour-pencil of white or red chalk, or crayon; or, again, with certain soft metals—lead, antimony, &c. The resulting marks are the brighter in proportion as the surface is rougher; but they are not durable, being easily rubbed or brushed off. The only way to fix them is to apply a fixative, such as a weak solution of resin in ethereal oils or volatile solvents, which dries on and in the substratum, and covers the colour with a protecting layer or film.

In *painting*, the colour and vehicle are intimately mixed together, and applied together upon the material to be painted, the colour being fixed on the painted surface by the "drying" of the vehicle, which has to some extent penetrated into the material.

1. Painting

Painting may be divided into two classes, *industrial* and *artistic*—a distinction, however, of little importance, so far as our technical treatment of the subject is concerned, since in both cases the method of painting is fundamentally the same, even though a number of refinements have been introduced into the higher branch.

a. Painting in Oils

The most important method of painting, both for industrial and artistic purposes, is *painting in oils*, because it gives the most durable results. A number of oils have the property of drying in the air and forming a viscid, gummy mass, which afterwards becomes more or less solid. According to recent investigations, this transformation consists of two phases: first, *an oxidation, i.e.*, an absorption of a ponderable amount of oxygen from the air; and, secondly, *a polymerisation, i.e.*, a condensation of the molecules.

The most important *drying oils* are, first and foremost, *linseed oil*, then *wood oil, nut oil, poppy oil*, and *hemp oil*. For industrial purposes only the first two are used; for artistic painting the last-named is sometimes employed, though wood oil is only very seldom used in this branch.

If the raw oil were mixed with the colours and applied to the surface to be painted, the drying process would, it is true, proceed, though much more slowly, but the thin oil would penetrate more or less extensively into the material (according to the nature of the latter), and thus separate from the colour. This would, on the one hand, result in a more perishable coating, partly deprived of its vehicle, and, on the other hand, the oil would form objectionable greasy lines on the contours of the painting.

In order to avoid this, the raw oils are made into *varnishes* for use in painting. Varnishes are drying oils which, by exposure to temperatures between 150° and 320° C. (sometimes assisted by added resins or metallic compounds) are converted into a viscous and partly oxidised and polymerised condition, in which they not only dry better and more quickly, but also form a more effectual envelope for colours and a more workable paint. The metallic compounds used in varnish-making are lead compounds (lead oxide, litharge) or manganese compounds (manganese hydroxide, manganous borate), also salts of fatty acids and resinates, a distinction being drawn between *lead varnishes* and *manganese varnishes*. The consistency of varnishes can be modified at will, the viscosity increasing with the duration of boiling. Concentrated compounds of lead or manganese with linseed oil (so-called soaps), which are then dissolved in oil of turpentine, have the property of accelerating the drying of paints. Such solutions—even the solid compounds, lead or manganese linolate, manganese borate—form part of the painter's stock-in-trade, as so-called "driers." Should the treatment with these substances make the varnish too thick, it can be reduced or thinned, chiefly with oil of turpentine.

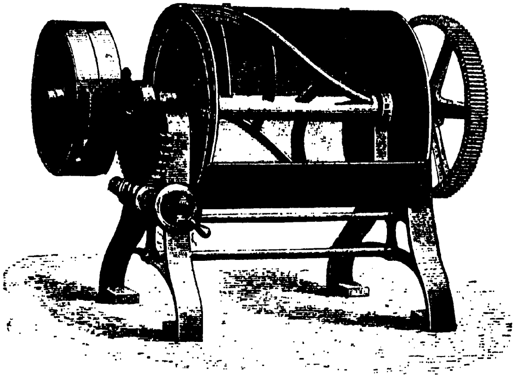
In boiling varnish care must be taken that the product turns out as light and clear as possible. A good varnish when spread on white paper should dry to a glossy, pale yellow, transparent coating, without any oily stain round the edges. Oil that has been overheated and overboiled, particularly with driers, gives hard and often blackish-brown varnishes, which are, of course, unsuitable for lighter paints.

In order to impart gloss to the paint, *lacquer varnishes* are used. They consist of a hard resin, particularly copal, dissolved in linseed oil varnish, and are then called *oil lacquer varnishes;* but when a volatile solvent is used—*e.g.*, alcohol, or oil of turpentine, acetone, benzene, &c.—a *spirit varnish* obtained. Varnishes of the former class are added to the paint itself whereas those of the latter are applied over the dried coating of paint.

For inferior purposes cheaper products, such as resin oil and mineral oil, are also used for making paint.

An important operation in the preparation of ready-made paint is the mixing of the colour and the vehicle. The old-fashioned method consisted in mixing the powdered pigment and vehicle by means of a broad, flat, handy tool—*e.g.*, a muller of suitably formed stone, china, glass, or earthenware—till a perfectly homogeneous paint was produced, the consistency of which could be controlled at will by the addition of more or less strong or thin varnish. This method, however, is only suitable for small quantities—*e.g.*, artist's colours and decoration work. Where larger quantities of colours are to be ground, machinery, often of a very complicated character, is used. These mills are classified into mixing machines and finishing mills, the latter converting the mixture of colour and vehicle into a perfectly uniform and impalpable mass, the particles in which cannot be detected with a magnifying glass.

FIG. 98.



The *milling* and *kneading machines* consist essentially of round or angular, vertical or horizontal receptacles, the mixing troughs, fitted with revolving stirrers, worked by hand or power. The varnish is placed in the trough and the stirrers (flaps) set in motion, the corresponding quantity of dry colour being then gradually added. When the mixing has continued for some time a rather crumbly, lumpy (or even slimy) mixture is generally obtained, in which colour and vehicle have been brought together into a tolerably uniform mass, but not yet smooth and finely divided.

Figs. 98 and 99 show mixers of this kind for large works. In recent years certain engineering firms who make a specialty of mixers for various trades have carefully studied the best form and most suitable disposition of the stirrers for different purposes. It is evident that a mixing machine will have a very different task to perform, for example, in mixing light amorphous lampblack with thin painter's varnish, and incorporating the heavy substance white lead with a mixture of linseed oil and dissolved resins (of the lacquer varnish type). Besides the power developed by the machine, its capacity for incorporating the components of the mixture as quickly as possible is also a matter for consideration.

FIG. 99.

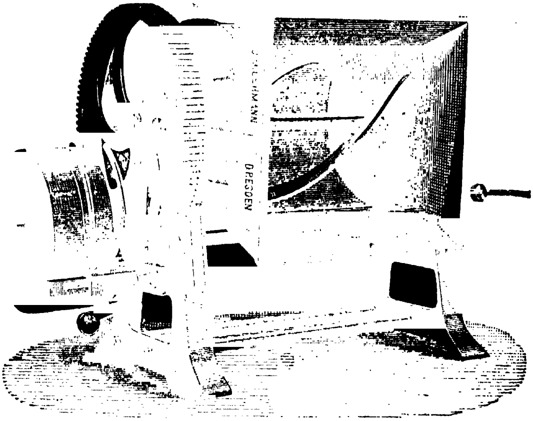
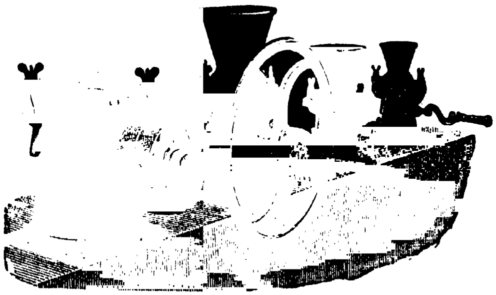


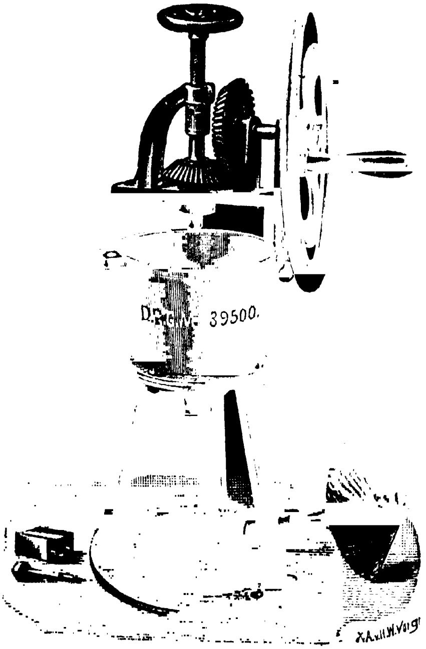
FIG. 100.



It is, of course, impossible to illustrate all the different forms of mixer used, and a few typical examples must suffice. The machines used fo materials that are specially difficult to mix are fitted with horizontal rotary stirrers, which also have a vertical up-and-down motion. The shaft carrying the mixing blades can be mounted on the wall of the workroom, whilst the mixing trough is formed of a wheeled truck, which conveys the mixed material to the grinding mills.

The mixers shown in Figs. 98 and 99 are fitted with tilting troughs to facilitate discharging the contents. In the position illustrated the whole trough is tilted forward 90 degrees. The mixing blades continue to run whatever the position of the trough.

FIG. 101.

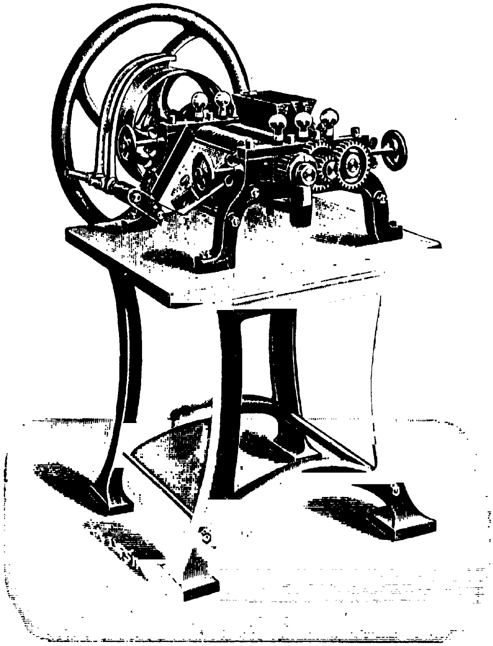


In ordering a mixing machine it is always advisable to let the maker know for what special purposes it is required.

From the mixers the mass is transferred to the grinding or finishing mills. These are either cone mills, in which the material is passed between conical grinding surfaces, or are roller-machines, in which the colour, after passing through a hopper, is distributed over long revolving rollers and ground between them.

The *cone mills,* illustrated in Figs. 100 and 101, are mainly used for more fluid, easily ground products, and mostly for small quantities only. For this reason they are generally worked by hand. Their working capacity is low in all respects, and their use is attended with certain inconveniences, since they are difficult to clean and have to be taken apart for this purpose. Hence they are only used in small works, and by painters who mix their own colours, though they are also preferred for making artist's colours that have already passed through the preparatory stage and

FIG. 102.

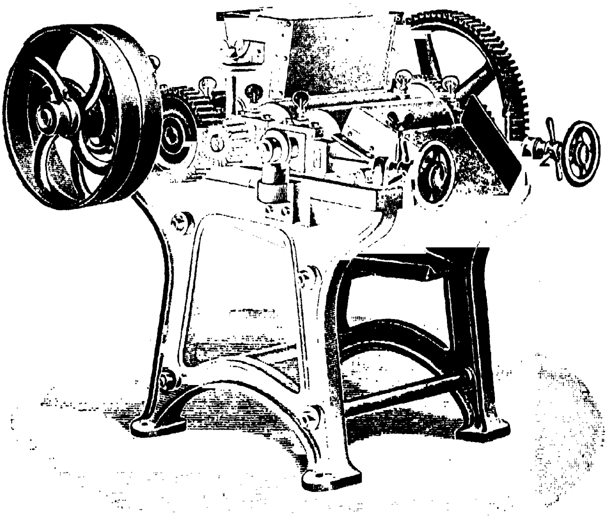


are ready for mixing with linseed oil to obtain the buttery consistency requisite for tube colours.

The construction of cone mills varies considerably. Round the bottom of the hopper is a fixed ring in the form of a crown, the lower grinding surface of which faces the movable grinding cone. The cone is turned to fit accurately against the stationary grinding surface, and the distance between them—*i.e.*, the fineness of the grinding—can be regulated by a screw. The colour forced out between the grinding surfaces by the rotation of the cone is removed by a scraper and collected in a channel. The hopper is sometimes fitted with a mixer, so that the mill will then serve a dual purpose. The mixing and grinding mechanism are operated simultaneously, but in the *Schmied cone mill* the mixer can be used by itself by shifting the drive on to a pulley for that purpose, the movement of the blades being reversed. The *Palmié cone mill* is made to work under atmospheric pressure, and is therefore fitted with air-tight joints. These machines, like those in which the material is pressed between the grinding surfaces by means of weights, have cylindrical hoppers.

For colours which must not be brought into contact with iron, mills are made with porcelain grinding surfaces; but the grinding surfaces have to be plane (not conical), and easily changeable.

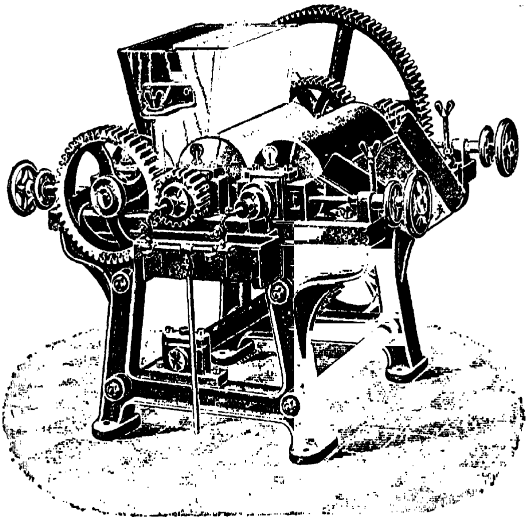
FIG. 103.



The cone mills may be driven from above or below. For certain purposes these mills are also provided with heating or cooling devices.

A far more important grinding machine is the *roller mill*. The simple form—*i.e.*, the two-roller mill—is, however, seldom used, the type generally employed being that with three rollers on the same plane. The rollers are of equal length and diameter, and run at different speeds by means of suitable gearing, the front or middle roller also receiving a reciprocal, horizontal motion, which increases the grinding effect. The rollers are either of iron (usually chilled castings) or stone (porphyry), according to the requirements of the material to be ground. For special cases hollow rollers are used, to be cooled or heated by a circulation of water or steam. Heating is rarely necessary in paint-grinding, though cooling is often desirable in the case of organic colours (lake pigments) which cannot without injury to their colour stand the heat always generated when the mills are kept running continuously. Cooling is often advantageous, too, when colours are ground with liquid vehicles (oil of turpentine). The material is fed into a hopper mounted in such a manner above the centre and back rollers that the mixed colour-pulp runs down between them, and is ground a first time. The centre roller then transfers the colour to the front one (second grinding), and the paint is taken off this front roller by a scraper, and runs down a shoot into a collecting vessel. Sometimes the hopper is fitted with a mixer, which is driven concurrently with the rollers.

FIG. 104.



The relative position of the rollers can be adjusted by means of hand-wheels (Fig. 102) to modify the fineness of the grinding; but it is essential that the rollers should be set absolutely parallel, or uneven grinding will result.

A small three-roller grinding mill, worked by hand, and mounted on a table, is shown in Fig. 102. Figs. 103 and 104 show the construction of heavy patterns for power driving, that in Fig. 104 being fitted with the cooling device already mentioned.

In large works which have required extension, grinding mills of various form and great power have been constructed.

Still more powerful machines are the types illustrated in Figs. 105 and 106. Fig. 105 represents a machine which really consists of three mills mounted one above another. Each set of triple rollers is arranged on a different plane, and in such a manner that the material issuing from the top set flows down direct on to the middle set, where it is again ground, and thence on to the bottom set, being finally discharged into the collecting vessel. The previously mixed colour is pumped up into the feed hopper, situated about 10 ft. above the floor level.

Fig. 106 shows an eight-roller mill. The feed hopper is mounted between the two centre rollers, and delivers the colour at both sides to the double set of four rollers, so that the machine is practically a double mill. The ground colour is discharged at both sides of the mill. There would be no difficulty in mounting the eight rollers in two vertical sets of four, or having two eight-roller systems one above the other, and thus obtaining larger and more powerful double mills. Machines of this kind are mostly employed in large printing-ink works for turning out "news" inks for rotary presses.

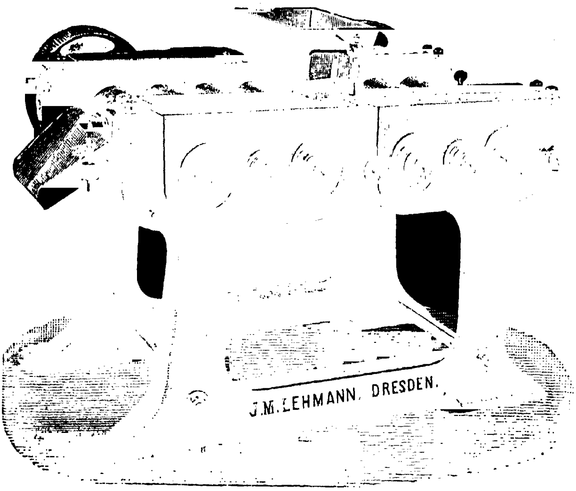
FIG. 105.

If, after having passed through the mill once, the colour is not yet sufficiently fine, it is put through the same mill again, the rollers being set closer together. Devices have also been constructed for automatically returning the ground paint to the feed hopper.

No definite figures can be given for the proportions of dry colour and vehicle. The determinative factors include not only the different specific gravities of the colours, but also the difference between the specific gravity of the vehicle and that of the pigment, as well as the purposes for which the finished products are intended, the method of application, and many similar conditions, and finally whether the colour is to be wholly or only partly finished.

We have noticed the mixing and grinding mills in the section on oil colours, because this is their special and almost exclusive sphere of practical application. Oils and varnishes are materials which will stand the heat generated by quick-running rollers, whereas water would evaporate very quickly and increase the difficulty of maintaining the consistency of the colours. The resins, soaps, waxes, and most ethereal oils compounded with oil in making different varnishes will also stand—and often require—grinding on hot rollers. In cases—*e.g.*, oil of turpentine—where this is not so, the cooling devices, closed hoppers, &c., already mentioned should be resorted to.*

FIG. 106.



The *chief vehicle used for ordinary paints* is linseed oil which has been boiled with litharge (boiled oil), or has acquired the consistency of varnish by admixture with certain varnish preparations or by thorough stirring and storage (raw oil varnishes). Boiled varnishes are generally preferred, chiefly because a cold-prepared varnish never acquires the slight viscosity and workable character of the boiled varnish, which causes the paint to distribute smoothly and regularly over the coated surface, and dries with a smooth gloss. On the other hand, cold-made varnishes are better preservatives when applied to porous materials, such as wood, than the boiled varnish, which remains more on the surface. Opinions, however, are divided as to the relative value of the two kinds of varnishes; and the fact that the varnishes themselves come from a large number of makers, and naturally deviate very considerably in their properties, renders definite tests and conclusions all the more difficult.

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* The grinding mills reproduced are made by J. M. Lehmann (Dresden) and G. Eckhardt (Leipzig), who are specialists in colour mixers and mills.

In order to improve the workability of paints, they are thinned down with oil of turpentine. Oil lacquers (copal, amber, dissolved in linseed oil) are added to increase the gloss; and wax and similar bodies are used to produce a matt effect. For common work resin oil, and even petroleum, are mixed with the varnish, though at the expense of the durability and appearance of the paint.

The *vehicles used for artist's colours* are, besides linseed oil, such drying oils as hemp oil, nut oil, and poppy oil. Artists have their own ideas as to the advantages of using mixtures of the various oils and adjuncts, such as wax, lacquers, driers, &c., for various kinds of work, and then applying such mixed colours by their own methods, a great deal of pother being often made about the "secrecy" of the whole affair. The adjuncts also differ with the various colours. Oil is by far the most important vehicle for artist's colours, the reasons for this preference being threefold. First of all properly selected and prepared oil colours give the most durable paintings; secondly, the artist's task is easier, because when working in oil colours he is enabled to judge the effect of the picture whilst still unfinished, the shade of the colours being the same in the wet state as they will be when dry; finally, oil is the only medium enabling the colours to be applied side by side or superimposed—*i.e.*, as transparent or opaque colour—without a change of vehicle.

The durability of oil pictures is explained by the fact that the oil vehicle remains in its entirety when dry. As already stated, the oil dries in the air by an oxidising process without evaporating. The vehicle occupies the same space when dry as it did in the fresh colour, so that no alteration occurs in the interior of the colour layer, as is, for example, the case with water colours, where the whole of the water evaporates, and the cohesion of the colours is lessened, particularly when laid on thickly, and a tendency to peel off and crack results. True, cracks are also formed in oil paintings; but this is generally due to defective methods of painting, or the exposure of the pictures to detrimental influences. Thus, when driers rich in oil of turpentine are added to the pigment, the partial evaporation of the oil of turpentine and the artificially accelerated drying have an injurious effect. Similarly, the durability of oil paintings is lessened if they are exposed to an alternately dry, cold atmosphere and one that is warm and moist, or are frequently exposed to the direct rays of the sun.

Like all organic matters, the dried vehicle (linoxin) of oil paints is unable to withstand all atmospheric influences permanently. Besides cracking and wrinkling, a dulness and spottiness of the painting are sometimes observed. The colours also gradually darken, and the vehicle perishes and separates, in the form of scales and powder, from the underlying surface, the colour, of course, coming away at the same time. To prevent this, attempts are made to protect the paint by a coating of resinous varnish, which is easily removed when perished, and can then be replaced by a fresh coating. On the other hand, *regeneration processes* have been devised on the basis of *Pettenkofer's* method, the cold vapours of alcohol or ethereal oils in closed cases being allowed to act on the surface, or the painting is "fed" by resins (especially copaiba). *Büttner Pfänner zu Thal* has extended this process by treating the pictures, before the vaporising process, with a mixture, *Phœbus A*, consisting of copaiba, vaseline oil, and ethereal oils, the vaporising treatment being then applied with oil of turpentine, chloroform, and camphor.

Further particulars on the regenerative treatment of oil pictures can be found in the pamphlets on this subject by *Pettenkofer* (Fr. Vieweg und Sohn, Brunswick) and *Büttner* (Staegmayer, Munich).

Certain special oil colours may now be mentioned. The *resin-oil colours* contain, besides linseed oil, a copal or amber varnish; also copaiba or Venice turpentine and similar resins. The resin-oil colours, among the best known of which are the so-called *Mussini colours*, are highly appreciated for drying smoothly and clearly without wrinkling. They are, however, far more difficult to regenerate than oil colours.

Ludwig, the well-known artist, invented *painting with petroleum colours*, which contain petroleum (boiling-point 275° to 375° C.) in addition to varnish and linseed oil. The effect of this addition is to soften the colour, make it more easily workable, and also to retard the drying process, so that the painting remains moist for a long time if kept in the cold. Should the picture then dry, Ludwig advises that it should be exposed to moderate warmth. Whilst the mineral oil unquestionably imparts greater softness to the colours, the second factor—namely, the drying capacity of the colours and the control according to temperature—seems to be based on a sophism. Mineral oils do not "dry," and oils of over 275° C. boiling-point evaporate only very, very slowly, if at all, even when gently warmed. When there is only a little petroleum in the colour, and the latter is inclined to dry quickly—say from the presence of driers or a lead colour—the petroleum will probably be harmless, since it penetrates into the substratum or is enveloped by the drying film of paint. On the other hand, a large quantity of petroleum in slow-drying paints will certainly be a defect in any circumstance. The so-called *enamel colours*, chiefly sold for ordinary painting, dry with a very high gloss, and to a certain extent imitate enamel. They acquire this property through a particularly high proportion of resin (copal, amber, &c).

As the oil colours dry with a certain gloss, they are unsuitable for decoration of large surfaces, because the dazzling reflected gloss makes the inspection of such a painting impossible. For such purposes the *oil-wax colours*, invented by *Andreas Müller*, of Düsseldorf, are suitable, and these also find application for paintings. They have a dull lustre, and are equal in durability to the oil colours.

The application of these oil-wax colours, however, is less simple, inasmuch as they do not dry with the same intensity shown in their fresh state. Lighter colours become brighter, but dark colours are darker and duller when dry, though they do not darken afterwards or show any tendency to crack.

The colours for artistic and industrial painting are sold in both the dry and ready-mixed form, the latter preponderating.

Many artists and painters are accustomed to grind their colours themselves with the vehicle, and the former especially observe a great deal of "secrecy" respecting the proportions of the main vehicle and the adjuncts. Almost every one has his own system, which he exercises personally and keeps strictly secret. Owing to the defective knowledge generally prevailing in artistic circles regarding the chemical and physical properties of colours, vehicles, &c., many of these methods are of highly problematical value, and it is a very regrettable fact that many important art productions suffer most grievously from the wrong treatment and application of the painting materials, and soon lose the brightness and intensity of the colours, crack, darken considerably, and peel off. An example in this respect is afforded by the beautiful works of the great Viennese painter *Hans Makart*.

Of equal importance with the correct choice and treatment of the colours and vehicle is the consideration of a suitable painting surface, it being essential that the material used in painting and that on which the paint is applied should be mutually suitable, whether artistic or industrial painting is in question. Though these purely practical considerations were formerly neglected by artists, endeavours are now being made to urge their importance upon them when students. Chemical experts have treated these questions minutely by valuable contributions to the professional press and in the form of special treatises,* and special instruction is given by competent professors in art schools and academies.

The German society "Die Deutsche Gesellschaft für Beförderung rationeller Malverfahren" at Munich has been occupied for years with this subject, the leading members being distinguished chemists who have devoted much thought to the chemical and physical basis of the question, How and with what shall one paint? And, thanks to their influence, a teaching centre and an experimental laboratory for all questions pertaining to the technics of painting, the Versuchsanstalt und Auskunftsstelle für Maltechnik, has been established by the Bavarian Government. The above society has also compiled a scale of *normal colours* for oil painting which experience has shown to be the most reliable and permanent under the unavoidable influences of light, air, and atmosphere—provided, of course, that they are properly manufactured, are perfectly pure and unadulterated, and are used in a proper manner. The colours are as follows:

White lead, zinc white,† Naples yellow, cadmium yellow (darker shades), Indian yellow, yellow and brown ochre, terra di Sienna, burnt ochre, red ferric oxide colours, vermilion, madder (alizarine) lake, cobalt blue, cobalt green, ultramarine, the various Prussian blues, chromoxide green, green earth, umber, asphalte, mummy, ivory black, lampblack.

These colours are, especially for oil painting, the most reliable, durable, and most uniform in themselves.

The German Association of Painters also recommends its members to pay greater attention to the quality of the materials, and has acquired a central experimental station in the laboratory of *Dr. Amsel*, in Kiel.

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* For instance, *Die Malerfarben, Mal u. Bindemittel u. ihre Verwendung in der Maltechnik*, by Dr. Fr. Linke (Stuttgart, P. Neff, 1904); "Malerbriefe," by Prof. W. Ostwald (*Beiträge zür Theorie u. Praxis der Malerei*) (Leipzig, Hirzel, 1904); *Techniken der decorativen u. monumentalen Malerei und des Anstriches* (München, Meyer, 1905); and many others.

† Antimony white must also be classified here. See remark at p. 290. [TRANSLATOR.]

These general remarks about oil painting are also applicable to all other points in the technics of painting, to which we shall revert later.

The antithesis of painting in oils is

b. Water-colour Painting,

which is suitable for industrial as well as for artistic purposes, and makes use of a great variety of colours in a multiplicity of ways. The colours for water-colour painting are ground or mixed together with watery vehicles, ready for use, and diluted with water when necessary.

The simplest form of water-colour painting, which is exclusively exercised for artistic purposes, is *painting in water colours—aquarelle.* The vehicle is a solution of gum arabic in water. The resulting colours are divided into two main classes: transparent colours, for *water-colour painting* in the narrower sense, and opaque colours, for *guache painting.* The disadvantage of water-colour painting is that colours once put on cannot be removed so as to allow of the surface being repainted, the colouring particles being held firmly in a layer of the vehicle on the painted surface, while they also remain soluble in water even after drying. The shade of colour also changes very considerably in drying, especially in thickly covered parts, the tone becoming duller and lighter.

Water and guache colours are treated with small quantities of diluted *ox-gall solution,* which fulfils the purpose of helping the distribution on the painting surface (paper, &c.), especially if somewhat greasy, and, on the other hand, prevents the water colours running together in small drops. The ox-gall, in fact, lessens the very high surface tension of the water, which is the cause of this tendency.

Besides gum arabic, dextrin, tragacanth, white of egg, and honey are also used as vehicles (soluble in water) for water and guache colours; and the prepared colours are named accordingly. Distemper (or size) colours are largely employed for industrial use, and also for high-class and even artistic decorative painting. Both ordinary glue size and the purer gelatine are used as vehicles. As the size merely thickens in cold water, but does not dissolve, it must be boiled until it no longer shows a tendency to set hard on cooling. The same result may be obtained by heating the size with acetic acid, nitric acid, or zinc sulphate on the sand-bath, in which case colours sensitive to acids (white lead, ultramarine) are, of course, out of the question. The so-called *Pereira colours* are prepared with isinglass dissolved in acetic acid.

The most suitable size is made from hides or leather, and it must be dry and free from any objectionable smell. Dark glue can only be used for dark colours the tone of which it does not hurt. To prevent the putrefaction of weak solutions of size or ready-made size colours salicylic or carbolic acid is added.

Artificial sizes—cold sizes—which are mostly of vegetable origin, are sold as substitutes for size. Of these the glue made from potato starch is a very useful form, especially when mixed with true size. The other artificial sizes are mostly prepared from starch.

Apart from the use of unsuitable brands of size, the appearance of size spots and the peeling of the painting arises from too large a proportion of colours or from painting on an unsuitable ground. The surface to be painted should be freed from old distemper and washed with soap and water. Exposure to strong heat (flue walls, &c.) will also cause the size colour to peel off. Gypsum walls and ceilings are primed for size painting with a strong solution of alum, to which a little size is added.

Water colours are sold in a dry state in the form of small globules, cakes, &c. (Indian inks, &c.), or in a semi-liquid condition (moist colours) packed in little cups or tubes. To retain this moist condition a little glycerine is added to these colours. Generally speaking, all colours are suitable for the preparation of water colours, bearing in mind, however, the exceptions already given in the case of acid vehicles.

In order to remedy the defect, already mentioned, that water colours cannot be painted over because of their solubility, various devices have been proposed. White of egg laid on thinly and exposed to the light becomes very sparingly soluble. When solutions of size, gum, dextrin (or colours ground in such solutions), are treated with a very weak solution of potassium bichromate, the resulting colours become totally insoluble in water. The applied colour can also be treated with formaldehyde vapour for the same purpose.

Belonging to the water-colour group is *Indian ink*, which consists of a size prepared from fish and leather incorporated with very fine lampblack and other ingredients by a secret process. It is scented with camphor and musk.

c. Tempera Painting

was a term originally applied to paints with mixed vehicles, but it is now used indefinitely for a number of methods.

Generally speaking, we now understand by tempera such vehicles as can be diluted, in a fresh state, with water without necessarily forming a complete solution, but which when dry are no longer soluble in water. In a certain sense they include the size and egg-albumen colours treated with potassium bichromate or formaldehyde, as already mentioned under water colours.

Liquid and more or less solid materials which can be mixed with water so as to become a uniform fluid, without passing into solution, are said to form an "emulsion." The formation of such an emulsion is a characteristic feature of the tempera colours. A good example is afforded by milk, which has also been used as an addition to colour vehicles.

The *Lechner oil tempera colours*—the use and advantages of which are described in a pamphlet, possess the special feature of not darkening as oil colours usually do. Further, they dry slowly and without any gloss. They are also of excellent covering power and brightness, and give very full and clear tones, especially when varnished. They can be used on all surfaces, and form a good substitute for oil colours.

In *egg-tempera* the yolk, which contains a colourless oil in the form of an emulsion, is stirred and beaten up with linseed oil. With water this mixture forms a stable emulsion that can be diluted at will. It makes a good vehicle for colours, and produces effects very closely resembling those of oil colours. In the egg-tempera the white of egg is also sometimes applied, and the vehicle is rendered more fluid by an addition of acetic acid, the mixture being then strained through a cloth in order to exclude the loose cellular matter. Egg-tempera is not very durable, and in decomposing liberates sulphuretted hydrogen from the sulphur contained in the white of egg. Hence lead and copper colours are unsuitable for this class of paints. The egg-tempera colours dry with a semi-gloss—*i.e.*, they are less glossy than oil colours, but more so than water colours.

Another important vehicle for tempera painting is *casein*, the curd separated from skim milk when treated with an acid. When treated with water and alkali (ammonium carbonate, lime-water, borax solution), casein gives a thick viscous size (casein glue), which does not gelatinise. It may be used as a vehicle for colours, and becomes insoluble in water when dry. Casein paint applied to freshly-cleaned plaster surfaces gives casein-lime tempera, well adapted for fresco painting indoors; in the open air, however, the paintings are not proof against the influence of the weather (*Gerhardt's casein colours*).

When this egg-size and casein-tempera, or gum mucilage or white of egg, are well mixed and stirred together with linseed oil, poppy oil, nut oil, resin, fat copal-lac, Canada or copaiba balsam, turpentine, &c., an emulsion tempera is obtained, which can be diluted with water as desired, and furnishes a very durable and bright coating. It is evident, therefore, that the tempera colours can vary in composition to an extraordinary degree, and the same applies to their mode of application—on paper, wood, canvas, surfaces primed with oil or size, and fresh lime plaster.

In the tempera emulsion the grains of colour are bound in a twofold manner by two vehicles, the oleaginous and the soluble, the honeycomb structure imparting special tenacity. The risk of cracking is consequently minimised.

The ready-made artist's oil colours sold in tubes are mostly prepared as pure varnish colours, seldom as "tempera colours." In order to prevent the separation of the colour from the vehicle, inspissating preparations—for example, wax, resin, &c.—must be added to the oil, especially in the case of specifically heavy colours.

d. Mineral Painting

In mineral painting only mineral colours and vehicles are employed. The three styles are *fresco painting*, the *al secco painting*, and the *stereochrome process*. These may be regarded to a certain extent as branches of water-colour painting, water being always applied as the diluting agent.

Fresco painting is one of the oldest styles, in spite of its difficult execution and the very limited form of pictorial expression. The colours are ground in water and applied to a surface of fresh lime plaster (*al fresco*). They penetrate to some extent into the surface of the mortar on the one hand, and on the other hand they are covered by the efflorescent lime stratum, with which they combine while the mortar is hardening in the air. Lime mortar consists of slaked lime mixed with sand. On exposure to the air this mixture parts with its mechanically retained and chemically combined water, and the calcium hydroxide is converted into calcium carbonate by absorbing carbon dioxide from the air, thus setting to a hard layer with the sand. During this process the water from the interior of the mass, and still containing calcium hydroxide, migrates toward the surface, and deposits here a thin layer of calcium carbonate—*i.e.*, on the top of the colours, that have partially penetrated into the mortar. Hence the dried colours are somewhat lighter in tone than when freshly applied—a fact that the painter has to take into consideration. At the same time he must take care to choose only such colours as are absolutely fast to lime—*i.e.*, fast against the alkaline action of the calcium hydroxide—and also resist the effect of light and air. The choice of colours for fresco painting is therefore limited to a few kinds. The chief mineral colours are ochre, umber, terra di Sienna, ferric oxide, red chalk, green earth, cobalt colours, ultramarine, indigo, and vermilion. Of the coal-tar colours, brilliant green, malachite green, naphthol green, naphthol yellow S, azarin red S, and others are employed.

A thoroughly dry wall that cannot absorb any ground water is covered with two thin coats of mortar, which must be allowed to dry in succession. The third or topmost layer represents the actual painting ground (*intonaco*), and of this only as much material is prepared and applied to the masonry as the artist can paint within a few hours. As soon as the exuding water begins to deposit the dissolved lime in the form of a crystalline film, the painting ground is no longer fit for use. The surface which remains unpainted at the end of the day's work must therefore be removed; and similarly the only way to make any correction in the painting is by cutting the portion of surface in question out of the picture and re-covering it with mortar. On hot days the work must not be continued for more than about four hours after the mortar is in position; in cool and damp weather a whole day. The total thickness of mortar is about 2 ins., but sometimes only ½ in. Freshly slaked lime is unsuitable for preparing the mortar; in fact, the longer the lime has been stored in the pit (two to three years) the better it is, the storage eliminating the dissolved salts (sulphates) which are detrimental to the painting. The sand must be quartz or marble sand, free from clay, and be previously washed with water. The ratio of slaked lime to sand depends on the "fatness" of the former, and fluctuates from 1 : 2 to 1 : 4.

Fresco paintings are more durable in mild climates than in higher latitudes, frost having a detrimental effect, so that frescoes on walls with a northern aspect are quickly spoiled. Walls with an eastern aspect are preferred, those which are situated in halls or covered courts being still better.

Al secco painting is performed with mineral colours on a smoothly cleaned dry lime-mortar ground. It is more convenient and easier than fresco painting, but does not give such durable results, and is quite unsuitable for the open air.

Sgraffito painting is not painting in the proper sense of the word. It consists in applying a dark brown or black coat, which is then covered with a white layer of lime. The design is drawn on the white coat of lime, and the surface is then suitably scraped so as to reveal the dark background underneath; this is covered with the clear colours forming the picture.

Ordinary *lime washes* for houses, walls, &c., are merely slaked lime coloured by pigments which are fast to alkalies and mixed with water ready for use.

The *cold-water paints*, for ordinary uses, sold in the trade are either preparations of silicate or mixtures of powdered colours and dry casein. They can be toned with other pigments, and merely have to be mixed with water, enough being made up at a time for one day's work. These paints dry dull, like wax paints.

The so-called *silicate paints* consist of a basis composed of dry sodium or potassium silicate, pumice stone, slaked and dried caustic lime, light spar and felspar in a very finely powdered state, and mixed with lime-proof colours for use.

Stereochrome painting was invented in the middle of the last century by *Fuchs* and *Schlotthauer*, of Munich, and employs silicates as a vehicle for the colours and priming. This style has also been cultivated by *Kaulbach*, and recently improved and extended by *Keim*, whose process is described in the publication *Keim's Mineral Painting*. In this new form the stereochromic process is decidedly superior to fresco painting in durability. First a layer of cement lime mortar about $\frac{3}{4}$ in. thick, is applied to the brick wall, and then covered with a priming layer $\frac{1}{8}$ in. thick, which is supplied by the *Steingewerkschaft Offenstetten*, in Munich, for use when mixed with water. Both these layers must be well dried before painting is begun. In order to remove the objectionable film of calcium carbonate formed in drying, the surface of the priming layer is repeatedly treated with dilute hydrofluosilicic acid and soaked with water. The calcium silicofluoride thus formed penetrates the coat of mortar, and afterwards forms insoluble compounds with the potassium silicate used for fixing—a reaction which imparts permanence to the colours. The latter are mixed with substances capable of forming the insoluble compounds in question, such as magnesium hydroxide, alumina, zinc oxide, &c.

During the progress of the painting the surface must be kept well moistened. The finished picture is left to get quite dry, and is then fixed by repeatedly sprinkling (with a syringe) the surface with a hot silicate solution, specially prepared for this purpose with caustic lime or ammonia, so long as any more solution is absorbed. The fixing process must take place in dry weather. Finally the surface is treated with ammonium carbonate.

The materials for the whole process are supplied by the firm mentioned above. Of course, in view of the chemical action of the hydrofluosilicic acid, the lime and the silicate, a suitable selection of corresponding colours must be made: for yellow, uranium yellow (barium uranate); for red, chrome red mixed with red lead; for blue, cobalt blue; for white, zinc white and artificial barytes. Zinc yellow, various kinds of ochre, violet and brown iron oxide are also used. The Keim colours are supplied as a thick paste, and must be diluted with water.

The *encaustic painting* of the ancient Greeks and Egyptians consisted in representing portraits on wood, ivory, and also stone, by means of wax coloured in the mass on the painted places. A kind of "filling up" (cestrum) was used for this purpose, and the drawing was first executed in black, papyrus ash being used as the pigment (monochrome painting), the colours being applied later. The most suitable wax for this purpose is said to have been Punic wax. According to *Pliny*, the wax was applied cold with a brush (no doubt in the form of a solution), the drawing and painting of the wax coating with the cestrum coming next, and the colours in the wax coat being afterwards fixed by heat. In later practice the colours were stirred in melted wax and applied hot.

The discoveries made especially at Herculaneum and Pompeii have shown that these encaustic paintings are more permanent than any others, many of them still retaining their pristine freshness, whilst frescoes and other styles have long since fallen into ruin.

Attempts have recently been made to revive this process, which was abandoned in the earliest middle ages on account of its complexity, and Professor *Cordenon* has invented liquid wax colours which, diluted with petroleum or analogous dissolving agents, are said to be suitable for durable paintings even on the northern side of buildings. The colours are painted on plaster prepared beforehand with a special liquid, which is essential to the success of the painting. The process can be applied to yainting on boards or plates, and painting on canvas, cardboard, paper, which must, however, be primed with chalk or plaster and size.

For special purposes the *blood* of oxen and pigs has been used as a vehicle, and, when diluted with water and mixed with freshly slaked lime, is said to give a particularly durable and waterproof coating on wood. This class of colour is used specially in China for painting packing cases for shipment abroad.

Pastel painting is another important style, differing from all the other kinds treated of hitherto, inasmuch as the colours are not laid on with the brush in a liquid vehicle, but applied as a solid material in the form of crayons. In this manner the drawing and painting of a picture are combined in one operation. The preparation of pastel crayons is the same as that of ordinary lead pencils.

The ancient painters used thin leaden rods for making their drawings, and it was only in the seventeenth century that the lead pencil began to be used in its present form, though the application of plumbago for writing and drawing is of much older date. At Borrowdale (England) a plumbago mine, opened in 1664, furnished a blacklead specially adapted for writing purposes. The price rose to a great height, and large quantities were exported, but the supply soon became exhausted. In the year 1795 *Conté*, in France, and *Hardtmuth*, of Vienna, simultaneously invented the mixture now used in the manufacture of pencils, and supplanted all artificial mixtures hitherto employed. The modern lead pencil is made of a mixture of the finest levigated clay with the finest levigated plumbago, thoroughly ground in mills and afterwards calcined in drums. This colour varies, according to the combination of the mixture, from deep black to greyish black; and the relative hardness can also be modified by the treatment employed. The levigated mixtures are filled into cylinders with a perforated bottom. A plunger forces the plastic mass out in the form of thin rods through the openings in the bottom. The rods are laid on boards, calcined out of contact with air, and then enclosed in wooden covers. Plumbago is at present obtained from Ceylon, the United States, and Great Britain.

If plumbago is replaced in the clay mixture by vermilion, Prussian blue, ultramarine blue, green earth, and other mineral colours, or also by mixtures of lakes, *coloured pencils, pastel crayons,* are formed in unlimited gradations of tints. In order to bind the mixture more thoroughly, gum arabic, size, or isinglass is added to the mass, the content of clay being reduced.

The colours applied in pastel painting are only mechanically retained on the painted surfaces, the colour mass being itself held together by a vehicle, but not attached thereby to the painting basis. Since shock or friction, &c., would dislodge the colour, this must be protected by varnishing the picture with a thin solution of resin, a weak spirit varnish, a 1 per cent. solution of shellac, or a solution of gun-cotton in amyl acetate, the so-called *Zapon varnish.* Fixed in this manner pastel pictures are perfectly durable, and if stable colours are used for the crayons the permanence of the pictures—any mechanical damage, of course, excluded—is only limited by that of the materials on which they are painted. A special feature of pastel pictures is that they retain their brightness, they do not darken, and, in fact, they represent the most durable products of the painter's art. Their sole defect is that the colours are not transparent.

An important champion of pastel painting is Professor *Ostwald,* at Leipzig, whose *Malerbriefe* (*Letters of a Painter*), already mentioned, deal extensively with the importance and execution of this style, and also give instructions, worked out by the writer, for manufacturing the crayons.

Raffaelli has invented oil colours for pastel painting in the form of painting pencils, which combine the advantages of oil painting with the convenience of pastel painting, independently of purely technical operations. These *oil-colour pencils* contain ready-made pasty oil colours, which do not dry in the pencil, and the applied colours, which can be eventually diluted by an addition of oil of turpentine, dry ineffaceably on the painting ground.

When dry coal-tar colours are added to a mixture of clay, plumbago, or lampblack, the so-called *ink pencils* are formed, which will write on moistened paper like ink. The writing produced by this means can be copied.

Mixtures of ordinary writing chalk, clay, and mineral colours or lake pigments form *coloured crayons* for drawing on blackboards for instruction and technical purposes.

e. Ceramic Painting

The sphere of ceramic painting comprises glass and china painting, the technique of which presents such marked peculiarities as to constitute them a special branch of artistic painting. The foregoing statement that pastel painting furnishes the most durable products must be understood in a limited sense as far as the organic ingredients of the picture (canvas, wood, paper, as painting basis) are concerned. Products of ceramic painting are of inorganic nature throughout, and therefore of unlimited durability, unless the painted object be completely broken or destroyed. Ceramic painting treats of the manufacture of coloured glaze, the colouring material of which must be able to resist the temperature attained in the melting of the glaze or the firing of the ware. For this painting—with which enamel painting must also be classed—only mineral colours are used, and even among these the selection is not a very extensive one. The technique of ceramic painting consists in applying the colouring matter on the body or ground—glass or china—in the form of coloured glazes, and then firing them together at a corresponding temperature. A coloured glaze of this kind has already been mentioned in the form of smalts when dealing with the cobalt colours.

The colours are mixed with a special melting body, the "flux," and with a vehicle of ethereal oil (oil of turpentine, essence of bergamot, oil of cloves, lavender oil, &c.), then applied with a brush, and left to dry slowly. The finished ware is then placed in the kiln and heated to temperatures sufficient to fuse the colour mixtures, but not the glass or the china forming the ground. The fluxes are therefore readily fusible glasses, compounded from red lead, borax, silicates, &c. During the firing process the oils used as a vehicle evaporate, the colour melting with the flux and adhering firmly to the painted substratum to form an inseparable whole. In china painting the colour is applied to the glazed china and fired on, since very many colours cannot stand the temperature at which the ware is fired. There are, however, certain so-called *high-glaze* ("grand feu") *colours*, which can also be applied under the glaze, and fired with the ware. The chief difference between glass and china painting is that the former requires transparent colours, whereas china painting is practised on a non-transparent white or even coloured ground.

White is formed by tin oxide and potassium antimonate; yellow by Naples yellow, iron oxide, lead chromate, barium chromate, silver chloride, silver oxide, silver sulphide, and antimony sulphides; red by iron oxide, a mixture of gold and tin oxides and silver chloride, red copper ore; black by platinum, cobalt, manganese, uranium, iridium oxides; blue by cobalt oxide, potassium-cobalt nitrite; green by chromic oxide, cuprous oxide, and ferrous oxide. The ceramic colours are mainly metallic oxides, and these are also chiefly used to produce the transparent colours necessary for glass painting, the less used metallic salts serving mainly for the opaline effects of china painting.

A number of metallic oxides already possess the colours which they should exhibit in the finished picture; but in many cases this colour is formed only by the process which furnishes the coloured glaze. This is particularly the case, for example, with cobalt and copper, the gold-tin-silver mixture, &c., the ingredients of the flux also influencing the result.

The term *glaze colours* is applied to such as are fused with a flux and then converted into a devitrified state for use, whilst *semi-glaze colours* are first produced in a semi-glazed state by aid of the flux before being used for colouring purposes.

2. Colours for Graphic Purposes

Besides lead pencils and coloured crayons already mentioned, this class includes *writing inks*, *drawing inks*, *stamping inks*, and *printing inks* of all kinds.

The pigments used are derived from all classes of organic and inorganic substances.

Writing ink is manufactured in a great variety of ways. The contained pigment, when of mineral origin, is in a state of solution or suspension, and dries on the paper unchanged, for instance, the mineral colours, most coal-tar colours and logwood inks. With other colours, however, certain logwood inks, some coal-tar colours, &c., the colouring matters change when brought on to paper, owing to the influence of the air or certain constituents of the paper. Finally, in many liquid inks the colour is only in a latent form, and is developed by the influence of air and light during and after drying—*e.g.*, the iron and gall-nut inks—or by the secondary influence of warmth or chemicals—*e.g.*, sympathetic inks.

Schluttig and Neumann give the following systematic classification of inks, according to their practical uses and composition:

1. Iron-gall inks.
2. Logwood inks.
3. Coal-tar colour inks.
4. Hectograph inks.
5. Mineral colour inks.
6. Inks from natural organic colouring matters.
7. Autographic (lithographic) inks.
8. Sympathetic inks.
9. Indelible safety inks.
10. Stamping and typewriting inks.
11. Drawing and endorsing inks.

The inks of the 1, 2, and 3 class are the kinds most generally used. They are subdivided into two classes, each according to its stability, the first comprising the iron-gall inks as the most stable, so-called *normal inks,* used exclusively for drawing up permanent deeds, &c., whilst the second class contains variously compounded, less stable products. Writing inks are either *ordinary inks,* which dry firmly and are then more or less insoluble, or *copying inks,* which permit the writings produced by their aid to be duplicated in the copying press. In the latter case the vehicle and pigment remain in a more or less soluble condition even when dry. There are two chief varieties of copying inks. *Wet copying inks* copy by placing a damp sheet of copying paper in contact with the dry writing, and then applying strong pressure, whereby the superficially dissolved ink is transferred to the damp sheet. *Dry copying inks* either remain for a time so far moist, without being effaceable, that they will give impressions on copying paper, or when dry are capable of being copied on to paper prepared with hygroscopic substances in a special manner.

All these writing inks are aqueous solutions of the relative pigments, to which gum arabic, sugar, dextrin, are added as a vehicle, their composition being often very complex.

The various inks are also sold in the form of powders or tablets, forming a mixture of all the dry ingredients, which merely have to be dissolved in water to be ready for use.

To the copying inks, in a wider sense, belong the *hectograph inks,* which are always solutions of coal-tar colours in a mixture of glycerine, water, and alcohol, assisted at times by acetic acid, without any vehicle.

Type-writer inks are special kinds of highly concentrated hectograph colours. Their preparation—in which the kind of ribbon used is of special importance—is a carefully guarded secret process. The colours are so highly concentrated that they appear dry at ordinary temperature, and will not easily rub off the ribbon. Non-copying typewriter inks are also manufactured as oil colours.

Mineral colour inks are little used except for fancy purposes—writing on dark-coloured paper. White inks are made of zinc white, finely suspended in a solution of shellac and borax. Blue ink is a solution of pure Prussian blue in oxalic acid. Green ink is prepared with an ammoniacal solution of copper acetate (blue ink that turns green in drying), or a hydrochloric or sulphuric acid solution of potassium bichromate reduced with alcohol. Red mineral inks are made of vermilion and red lead, yellow inks of orpiment, gold and silver inks of genuine and imitation gold and silver foil and bronze powders, mixed with gum arabic, alkali silicate, soluble glass, weak Dammar varnish, and similar vehicles.

In a similar manner, natural organic colouring matters (indigo, madder, cochineal, turmeric, annatto, saffron, gamboge, &c.) are mixed in the dry or soluble condition with gum solution to the consistency of writing ink.

Autographic and *litho transfer inks* are superfatted resin and wax soaps. They serve the purpose of protecting those places on the lithographing stone, which later are to transfer impressions on to the paper, during the etching of the stone with nitric acid, the fatty soap repelling the dilute acid, so that the places covered with the ink are kept intact and in a suitable condition for taking up the fatty lithograph ink, whereas the etched portions of the stone absorb water and repel fatty colours.

The main ingredients of these preparations are soaps, wax, tallow, mastic, asphalt, Frankfort black, turpentine, lampblack, and similar substances. The making of good lithographic inks, Indian inks, and chalks is a very difficult and complicated task, requiring a very accurate knowledge of the result of the various operations, long experience, and the greatest attention in order to obtain successful results.

Autographic litho transfer inks are emulsions of the consistency of writing inks, and enable the original handwriting to be transferred from the paper to the stone. Lithographic chalks and Indian inks serve for drawing and painting direct on the stone, and represent to a certain extent the concentrated form of the inks.

Sympathetic inks are invisible when applied on white paper and dried, the writing only appearing after a special treatment with chemical solutions, exposure to light, moistening, warming, &c., in various colours, according to the ingredients used.

These inks being of no practical importance, will not be further discussed, except to mention that the active ingredients are solutions of metal salts (cobalt, iron, &c.).

Indelible writing inks mostly contain, in addition to other colouring matters, carbon in the form of lampblack or lignite. As the carbon is insoluble in all liquids, and does not penetrate into the paper, but merely dries on the surface, the vehicles (gum-lac, shellac dissolved in borax, &c.) have to be specially selected. Aniline black and solutions of gold, platinum, palladium, iridium and vanadium salts, from which the corresponding metals are deposited in the paper and in fabrics—linen, for example—by reduction, form the material for indelible inks.

Stamping inks are either destined for metal stamps, and are then mostly oil or fatty colours, or they are used for rubber stamps, and are then water colours.

Oily stamping inks are made with mineral colours as well as fatty colours soluble in oil. The former are ground with boiled linseed oil, or with nut, poppy, or olive oil, and diluted to a workable consistency. The second class consist mostly of coal-tar colours, in a solution of glycerine, dextrin, and water. Lampblack, Prussian blue, &c., can also be used for these purposes. The aqueous stamping inks are solutions of tar colouring matters in water and glycerine, mixed with alcohol, acetic acid, &c.

Permanent marking inks consist of aqueous solutions of silver nitrate, or aniline chlorides and copper sulphate. The intensity of the black develops only on drying in the air, by exposure to light, or even by the influence of soap in washing.

Meat stamping inks are made of perfectly harmless colouring matters; for example, logwood extract with a solution of glycerine, or coal-tar colours soluble in fat with solutions of resin in volatile solvents (benzene).

The numerous *mimeograph* and *cyclostyle colours* now largely used for reduplication in quantity are fatty colours, the vehicles of which consist of mixtures of vaseline, mineral oil, linseed oil, rape oil, and similar bodies, whilst lake pigments, lampblack, Prussian blue, &c., form the pigments. The colour is ground to a thin paste, so that it can be pressed by the roller on to the underlying paper through the original sheet of wax paper, which is perforated by means of a special platen in the typewriter.

Drawing and *endorsing inks* are compounded, in a dry and liquid state, from organic and inorganic colouring matters with oily and watery vehicles in numerous ways. They are used for a great many purposes. As there is nothing novel in their preparation and use, we need not go further into the subject.

The far more important *printing inks* (lithographic and letterpress) are, with one exception, all fatty colours. The colouring principle of the black inks is almost exclusively lampblack of different qualities; whilst the coloured inks are prepared from all kinds of pigments, inorganic and organic, chemical mineral colours, and lakes from vegetable and coal-tar colours, provided they are sufficiently fine-grained to grind to an impalpable condition in the vehicle. In view of this essential condition, it is evident that a large number of known pigments are quite unsuitable for printing inks, whilst others, again, can only be used to a very limited extent.

In view of the very fine work now done in printing, it will be easily understood that the blocks used are of very delicate grain, especially those for half-tone work, the softness and delicacy of which are almost equal to those of the photographic negative, with the help of which, in fact, the blocks are produced. The printing surface is of three kinds—relief, flat, and engraved, *Relief printing* comprises typographic and block printing, the type or drawing to be printed standing out in relief on the surface of the printing plate, and only these projecting parts being reproduced in the impression. *Level* or *flat printing* is typified by the lithographic print. The parts of the stone to be printed from do not stand out on the plane surface, and are merely prepared so that they will take up the fatty colours, whilst the other parts of the stone have the property of repelling the colour. *Engraved printing* is the process by which copper engravings, steel engravings, etchings, &c., are produced. The drawing is cut deeply in the metal plate, so that when the whole plate is rubbed over with colour only the deeper parts are filled up, whilst the clean polished surface of the plate takes very little colour, and that is entirely wiped off before the impression is taken. A special quality of paper is required for this work—viz., one that will penetrate the recesses of the plate in the press and pick out the colour lying therein.

It will be easily understood that these various processes require inks of different properties. This is so as a matter of fact, but the chief difference is in the vehicle, the pigments for all processes being the same. Engraving work is the class that is least exigent with regard to fineness of grain in the ink, and the blacks (Frankfort black, ivory black) used for this purpose are useless for ordinary printing ink, even the most inferior kinds of news ink.

The choice of vehicles for printing inks is a somewhat limited one, and is chiefly confined to linseed oil, thickened to varnish by the action of heat. The consistency of the varnish ranges from a viscous liquid to a gummy-elastic substance, according to the heating process, a number of intermediate strengths being prepared as stock varnishes. The pigments are ground with a varnish of suitable strength for the class of ink desired, driers and adjuncts for improving the gloss being added according to requirements. For certain purposes, particularly for printing on rotary machines, linseed oil varnish is too tacky, and too dear, and has to be replaced by varnishes compounded of resin, resin oil, mineral oil, and other substitutes.

For cheque printing and other purposes copying inks are prepared by dissolving coal-tar colours in water and glycerine, dextrin, &c.—viz., something after the manner of the writing inks used for copying, only in a more concentrated state.

Similar to the graphic colours in the manner of their application are the *wall-paper colours* and the *colours for fancy papers.* Both are water colours made by the aid of a glutinous vehicle—rye-meal, dextrin, size, and similar mixtures. Colours for wall-paper printing are sold as paste in order to facilitate their use. Hence colours made by the wet process need not be dried for this purpose, and the only care is to see that the colours are supplied in a not too thick paste and always possess the same drying capacity. The colours are applied to the wall-papers by means of wooden rollers, on which the designs are cut in relief. The rollers may also be faced with copper, type-metal, or some flexible composition. The ground colour is applied to the paper by felt rollers. In making fancy papers the colours are laid on by hand or by machine with the aid of brushes, whisks, sponges, &c., and are then treated further in various ways (calendered, printed, embossed, &c.).

Cloth printing must also be briefly mentioned here. The colours are applied by the aid of square blocks in roller or flat printing presses operated by hand or power. Opaque colours (ultramarine, chrome yellow, chrome green) are used as well as dissolved colouring matters; *e.g.*, the coal-tar colours.

In many cases a combination of cloth printing and dyeing is practised by printing the material with a fixative which will then develop the colour component previously or subsequently applied (for example, Prussian blue, chrome yellow, &c.). Further, the method of producing lake pigments can also be employed, the fabric which acts as a carrier being printed with a mordant and then treated with the coal-tar or vegetable colouring matter.

Varnish and egg-albumen are also employed as a vehicle for the colours, the colour being fixed on the cloth by the coagulation of the egg-albumen.

The albumen used may be either fresh egg-albumen or that from blood, and mixed with starch, gum, and alumina. Casein and gluten are also in use as fixing agents, the former dissolved in alkaline liquids, the latter in alkaline and acid liquids. The selection of colours is of course confined to such as will stand acid or alkali.

In this method of printing, as in letterpress or ordinary printing, the adherence of the colours is merely superficial and depends on the vehicle only.

Calico is the fabric usually printed on, though linen (canvas), wool, and silk can also be treated in the same way. Except, however, where the colour is developed in or on the fabric, or is precipitated in the form of a colour lake, the printed impressions are not durable, but can be easily removed by mechanical means and weak chemical agencies; for example, by washing. Moreover, only very few of the lakes produced in this manner are fast to water.

In the foregoing pages we have given a general review of the methods of applying the colours otherwise than by painting. Of course, in each method there exist numerous modifications and adaptations to certain purposes intended for the attainment of certain artistic, technical, and sanitary effects. Just as in artistic painting the style and technique differ according as the work is destined to be hung in a gallery or for the exterior decoration of a building, so is it with industrial painting: the choice of colours, &c., for painting doors, windows, ceilings, furniture, &c., indoors will differ from those selected for decorating the outer walls, painting carriages, railway waggons, ships, &c., exposed to the influence of the atmosphere. Generally speaking, the vehicle which fixes the colour on to the painted object will also have to be considered, and care must be taken to choose and compound this in such a way that it may combine as firmly as possible with the ground surface (wood, metal, stone), and at the same time withstand the different influences acting thereon (damp, moisture, sunlight, foul air, &c.).

Hygienic considerations will also affect the choice of the colours for certain purposes. Colour works can only be established in accordance with the law and in this trade there are special legal requirements which have to be fulfilled. Fabrics, wall-papers, &c., for the decoration of living rooms, and colours used in the painting of toys, colouring of sweets, confectionery, &c., must be free from harmful ingredients; and the same applies to the colours used for the printing of wrapping paper for edibles, &c.

Sausages may be *coloured* with *azo* dyes, to which, however, some disinfectant (boracic acid, formalin) must be added, so that in the event of the meat undergoing decomposition the colouring matter will not be reduced and decolorised by the hydrogen evolved. For *cheese colouring* annatto and turmeric are used in alkaline and alcoholic solutions, which are added in small quantities to the milk. For *butter colouring* annatto, saffron substitute, and coal-tar colours are used.

Colours for coating stoves, heating apparatus, boilers, and similar objects which are kept continually at high temperatures must be able to stand a certain degree of heat, and colours for use in rooms in which acid gases or sulphureous vapours are liberated should be insensitive to the influence of these products.

Iron staircases and railings, bridges, roofs, &c., must be painted with colours possessing anti-corrosive properties. Paints (anti-fouling compositions) for the metal sheathing on ships' bottoms must not only resist the corroding influence of sea-water, but also destroy animal and vegetable parasites living therein.

According to the German patent 107237 (*Dr. Alexander*, of Hamburg), certain xanthogenates of the heavy metals exert this prophylactic action. The xanthogenates of copper and tin furnish, on decomposition, sulphides and hydrosulphides, which cover the whole of the ship's bottom with a protective film; this is continually renewed and acts as a violent poison on the flora and fauna of the sea. The xanthogenates mentioned are mixed with the paint either in a dry state or dissolved in carbon disulphide.

Bagg, of Vienna, recommends an addition of copper cyanide or copper sulphocyanide in anti-fouling compositions. Whilst some manufacturers depend on the directly poisonous action of the paint, and work in more than 50 per cent. of arsenic and over 30 per cent. of mercury, others discard poisons entirely, and claim greater efficacy for a solid, enamel-like layer, in which the colour sets hard, and by its imperviousness is said to prevent the deposition of organisms.

Luminous or *phosphorescent paints* consist of calcium sulphide, barium sulphide, and strontium sulphide, the illuminating effect of which is based on phosphorescence. The only one of practical importance is calcium sulphide (Balmain's luminous paint), which is largely used for painting street and house signs and dial plates. The luminosity is replenished by insolation during the day.

A very powerful luminous paint is prepared from calcium tungstate. According to the investigations of *Dr. Roth* and *Dr. Aufrecht*, the phosphorescence of the luminous colours possesses therapeutic value, inasmuch as it is fatal to bacilli and bacteria. In particular it is said to be possible to destroy disease germs by introducing into the interior of the human frame an apparatus that has been coated with luminous paint and exposed to sunlight throughout the day. Pus and cholera bacilli are said to have been destroyed in seven hours, typhus bacilli in eight hours.

According to a recent American patent, a luminous paint can be prepared from radium carbonate.

3. Dyeing *

In contrast to painting, in which, as we have seen, merely a superficial application of colour takes place, either over a part or the whole of the surface to be coloured, the process of dyeing generally implies the impregnation of the whole mass of the fabric or substance with colouring matter, so that the colour is not removed when the substance is peeled or subjected to similar treatment. True, this distinction is not invariably correct, for in many cases the processes are closely allied, though as a rule it will be found that in dyeing nearly the whole mass of the substance is treated with the colouring matter, whilst in painting only a limited superficial application of the colouring material occurs.

Moreover, the dyeing process is often directly combined with the actual formation of the dye-stuff in question, but this is never the case with painting.

We are already acquainted with the manufacture of fancy papers as the industry which supplies finished paper with a coloured surface. Another and different branch is the production of *coloured papers stained in the mass.* For this purpose both inorganic and organic colours can be used—*e.g.*, ultramarine, Prussian blue, chrome yellow, various kinds of ochre; and, on the other hand, solutions of vegetable colouring matters or of basic and acid coal-tar colours are added to the paper pulp in the paper-making machine before sizing, which latter operation fixes the colours in the mass. Stained papers are also made by the dipping process, in which the finished sheets are dipped in the solution of colouring matter and impregnated by the same. This latter process entails the use of colouring matters which are soluble in water—*i.e.*, principally those of organic origin.

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* See remark on p. 479. [TRANSLATOR.]

The most important dyeing process is that applied to *textile fabrics*, an industry pursued on a scientific basis and employing highly complicated processes. Here the inorganic colours have almost entirely gone out of use, except for the occasional employment of chrome yellow, Prussian blue, and copper sulphate. On the other hand, the vegetable colouring matters, which at one time held the field, have stood their ground to a certain extent, though restricted to a very insignificant sphere of application. At present the coal-tar colours are by far the most important materials used in cloth dyeing; and, in fact, it was to the cloth-dyeing industry that the enormous development of the coal-tar colour-manufacture owed its inception.

The theory of dyeing has been made the subject of very extensive investigations, in which science and practice have gone hand in hand; but thoroughly conclusive results have not yet been attained in all cases. In most instances the fixing of the colouring matter on the fibre must be regarded as a chemical reaction, whereby either the chemical composition of the fibre endows it with properties enabling it to enter into chemical combination with the colouring matter, or else it is prepared by a treatment with salts which impart this property. The conception that dyeing is a merely mechanical fixation (absorption, endosmose) has now been almost entirely abandoned. According to another modern hypothesis, the process is one of "solid solution"—*i.e.*, the solid material of the fabric holds the colouring matter in a state of solution.

It has already been mentioned that colouring matters which unite direct with the fabric are termed "substantive" dyes, because they are taken up from their solutions by the fibre without the latter having been subjected to any special treatment for this purpose. On the other hand, colouring matters which dye prepared fibres are called "adjective" dyes. This difference, however, is not strictly defined, because all fibres do not behave alike toward all colours. Hence a colouring matter which is "substantive" toward animal fibres is not necessarily so toward vegetable fibres, the former generally possessing a considerably greater affinity for colouring matters than the latter class.

Magenta is an example of a colouring matter that is substantive toward animal fibres. The dyeing process can be explained by the hypothesis that the fibre acts like an acid, decomposing magenta and taking up the colour base, with which it forms a dye salt. In other cases the fibre may act as a base—*e.g.*, when silk and wool are dyed with acid azo colours. Here the acid of the colouring matter must be liberated from its combination by means of a strong acid before the fibre base can combine with it to form the dye salt. This is usually effected with sulphuric acid or Glauber salt, or both together.

For practical purposes the classification of dyeing processes according to the kind of material to be dyed is the most suitable—viz., wool dyeing, silk dyeing, cotton dyeing, &c.

The technical performance of the process consists in bringing the fabric into contact with an aqueous solution of the colouring matter (the dye bath), and, with the assistance of stirring, working the material about, warming, &c.,

enabling the fabric to absorb as much of the colouring matter as is required to produce the intended shade of colour. Except in the case of substantive colouring matters, the material is prepared beforehand with mordants, which precipitate the colouring matter on the fibre in the form of a lake. As a matter of fact, the oxides and salts used as mordants are precisely those already mentioned as precipitating and shading media for the colour lakes.

Wool is dyed either "in the wool," "in the yarn," or "in the cloth." In the first-named case the wool is freed from the "grease" by scouring with soap and alkali carbonates. Many of the basic, acid, and benzidine colouring matters will dye the wool in a warm bath. In applying adjective colouring matters the wool is treated either in a warm bath containing the colouring matter and mordant at the same time (single-bath method), or is first mordanted and then dyed (two-bath method); or, again, the wool may be dyed first and treated with mordants subsequently. In certain cases—for example, in black dyeing with logwood—a mordant is used both before and after dyeing; and in order to improve the appearance and brightness of the colour a third brightening bath can be applied. Some colouring matters are fixed by means of finely distributed sulphur, precipitated on the fibre by a sulphuration process.

Silk dyeing is, on the whole, similar to wool dyeing, except that cold baths are almost exclusively used. The silk is dyed in hanks, previously scoured to remove the "gum"; and only certain kinds of silk are dyed with the silk gum on, in order to produce a certain solidity. After the dyeing process is completed the silk hanks are put through a gloss machine, over a system of rotating rollers, which improve the feel and softness of the dyed fibre. They are also put through calendering rollers, heated by steam. The black dyeing of silk is often made the occasion for artificially increasing the weight, the silk being treated with tannic acid and dyed with ferrous sulphate, by which means the silk can be loaded to two to four times its original weight, the product being, however, of inferior quality.

In *cotton dyeing* the yarn or fabric is first of all washed with soap and soda, and, when light shades are in question, is bleached, though this latter treatment is unnecessary for darker shades. Only a few colours of recent date will dye cotton substantively, and in most cases mordants have to be used. In order to approximate cotton and other vegetable fibres to the character of nitrogenous animal fibres, they are "animalised"—*i.e.*, impregnated with nitrogenous substances: egg-albumen, casein, size—and thereby enabled to take up the colouring matter more easily. The same effect is produced by treatment with milk and sodium stannate, followed by solution of alum, and finally by impregnation with silicates and subsequent treatment with hydrochloric acid. This deposits silica on the fibre, and enables the latter to convert basic colouring matters into insoluble salts.

In dyeing, two colouring matters of suitable chemical properties can also be made to react on each other, and thus fix themselves on the fibre. With this object the fibre is dyed first with an acid colour and then with a solution of a basic colour. Mixed colours and special shades can be obtained in this manner.

Linen dyeing is practically the same as cotton dyeing, but the processes and colouring matters suitable for this purpose are far less numerous, because linen has to be more frequently washed with soaps, &c., and therefore requires specially fast dyes.

Union dyeing is concerned with fabrics woven from mixed yarns. Half-linen, which consists of linen and cotton, presents no difficulties in the selection of process and colouring matters. With half-silk (silk and wool or cotton) and half-wool (wool and cotton) it is necessary to dye the two fibres separately before weaving, or, for example, to weave undyed silk with dyed cotton, and then dye the finished fabric once more.

By means of suitable processes the organic colouring matters can also be used for dyeing jute, feathers, hair, wood, moss, flowers, leather, size, soap, spirit varnish, wax, stearin, paraffin wax, fats, straw, vegetable ivory, buttons, &c. In such cases the materials of animal origin (feathers, hair, bones, horn, size, albumen, leather) behave in the same way as wool and silk.

For colouring varnish, wax, paraffin wax, stearin, oils, and fats the so-called *fatty colours* are used, which are soluble in the said materials, to form compounds of colour bases with stearic acid (stearates). Alkaline products of this kind are used for colouring soap.

Hitherto we have considered processes of dyeing with ready-made colouring matters; but, as in the manufacture of lakes, the *developing colours* may also be employed for dyeing fabrics and other materials. Turkey-red dyeing and indigo dyeing come under this category.

Turkey-red dyeing was formerly practised on cotton, wool, and silk with the aid of the natural colouring matter of madder root, but at present the artificial alizarine is used. In the modern process the yarn, boiled and washed with soda, is saturated with Turkey-red oil (a mordant product obtained by treating olive or castor oil with concentrated sulphuric acid, washing, and neutralising with ammonia), then dried and steamed. After treatment with alumina mordant, the yarn is dyed with alizarine solution, followed by repeated treatments with Turkey-red oil, steaming, and a process of purification in a solution of soap under pressure. In the older, very complicated and tedious white-bath process the yarn was repeatedly mordanted and dried with a mixture of "Tournant oil" (sulphonated olive oil) and sheep- or cow-dung dissolved in soda solution (the emulsion bath), then repeatedly washed with soda solution and dried. A treatment with a sumach solution and afterwards an alum solution followed next, this being succeeded by dyeing with madder and finishing with soap and stannate.

The colouring matter of *indigo* has no affinity whatever for animal or vegetable fibres, and the dyeing has to be performed by the vat process. Solvents being inapplicable, the indigo has therefore to be reduced to indigo white, which, when bodied on the material in the state of an alkaline solution, is reoxidised into blue by exposure to the air. The alkaline solution of indigo white is termed the indigo or blue vat. There are two different systems, cold-vat, and warm-vat processes.

The cold vats are either sodium hyposulphite vats, in which the sodium hyposulphite—obtained from acid sodium sulphite and zinc filings—is the active ingredient; or the vitriol vat, prepared from copperas and lime; or, finally, the zinc vat, prepared from zinc dust and lime.

The warm vats are also known as fermentation vats, because in them the hydrogen liberated by the fermentation of organic bodies constitutes the reducing agent. The blue dye (dyer's woad) vat consists of indigo, dyer's woad (blue dye), bran, madder, and slaked lime; the soda vat, of indigo, bran, soda, lime; the urine vat, of indigo, madder, urine, and common salt. The reoxidation of the indigo white to indigo blue is effected by the oxygen of the air. This process is also known as "fading," because the conversion into blue is preceded by a temporary green coloration.

The dyeings of textile materials are subjected to numerous tests. In the first place, they must offer certain resistance to the influences of light and air; and in many cases fastness to hot soap and water is required. Finally come fastness to rain, dust, and friction (wear).

Like paper, *glass* is also coloured in the mass. The colouring matters in this case consist mainly of metallic oxides and salts, as in coloured glazes and pottery painting. The pigments include especially iron (for yellow, red, brown, violet); manganese (grey and black); copper (as oxide, blue-green; as protoxide, red); cobalt (blue); silver (yellow); chromium (yellow-green); gold (rose to purple, ruby glass); antimony (gold-yellow); molybdenum (red ochre); uranium (greenish yellow); cuprous sulphide (sepia-brown). Tin ash, cryolite, bone ash, fluorspar are used for the manufacture of opalescent glass.

The coloured glass is either stained throughout the mass or coated with a coloured film (flashed glass). In this latter case a thick plate of colourless glass is coated with one or several layers of coloured glass. Flashed glass is used for polychrome designs on glass tablets, portions of the various coloured layers being removed by grinding thus exposing the under layers in bold relief.

Certain organic colours are also used for scientific purposes, the colour serving merely as a means to a certain end. Thus, in *volumetric analysis* the chemist uses certain colours which are bleached or change colour under certain conditions. Litmus is blue in alkaline solution, but turns red when the solution is acidified, so that by means of this indicator the conversion of the alkaline solution into the acid state, and *vice versâ*, can be instantly detected. Diphenylamine orange is yellow in alkaline solutions, but crimson-red in presence of acids. Similar applications are found for methyl orange, ethyl orange, rosolic acid, phenolphthalein, Congo red, &c.

In *microscopy* coal-tar colours are used for the identification of tissues, fibres, bacteria, &c., by the way in which these absorb certain colours thereby furnishing characteristic stainings. Saffron, Congo red, and methylene blue enable vegetable fibres to be recognised direct, whilst after treatment with tannin and tartar emetic the same result is obtained with methyl violet, Bismarck brown, malachite green, auramine, &c. Animal fibres are stained direct by methyl violet, magenta, auramine, in presence of sulphuric acid by methyl orange, magenta S, and some others.

Finally, the coal-tar colours are used in photography in the preparation of *isochromatic plates*, light-filters, &c. By the addition of some colouring matters—such as auramine, cyanine, quinolin red, erythrosine, &c.—the sensitiveness of the photographic emulsion is increased for certain colours, owing to the absorption of special light rays by these colouring matters. In this manner it is possible to reproduce reds, yellows, and greens in the photographic picture in their correct colour-values, which is impossible of attainment with the ordinary plate, owing to its inferior absorptive power for these colour rays.

We may also briefly deal with *photography in natural colours*, which since the beginning of the last century has formed an object of ardent research by men of science and photographers. The first to obtain satisfactory results was *Lippmann*, who made use of the interference rays. However ingenious his process may be, it did not lead to any practical success. Furthermore, the attempts made by *Seebeck* and then by *Verres* to prepare colour-sensitive photographic plates were not crowned with success. The silver sesquichloride used by them, however, fulfils the requirements of the case to a certain degree, but is not sufficiently reliable, though orthochromes of coloured transparent pictures can be obtained with an emulsion of silver sesquichloride and collodion by a very long exposure.

Herschel, Davanne, Wiener, and *Wallot* tried to attain their object with coal-tar colours, and based their processes on the fact that coal-tar colours do not fade in all lights, but only in a white light or one of special colour. Thus red colouring matters remain stable in red light, blues in a blue light, &c. *Worel* has continued these tests, and prepares a suitable colour mixture in an alkaline solution of primrose, Victoria blue B., cyanine, turmeric root, auramine, with an addition of 1½ per cent. of aniseed oil. He steeps writing paper, free from woody fibres, in this solution, and dries it in a dark room. The possibly fresh prepared paper is exposed to the sunshine for five to thirty minutes in a printing frame. The prints, however, fade entirely in about twenty days in diffused light, though when kept in a portfolio they will last for years. More recently *Dr. Neuhaus* and *Professor Miethe* in particular have developed this branch of photography, and the last-named investigator has obtained extremely valuable results.

These two investigators work chiefly with the bleaching system, with about thirty coal-tar colours and with chlorophyll, which latter influences the bleaching of the colouring matter. The colouring matters are used in a gelatine solution, and it is found that the kind of gelatine as well as the properties of the paper play a very important part in the bleaching process. A certain number of inorganic and organic derivatives have been found to be more or less sensitive. Professor Miethe has also manufactured colours that are particularly sensitive to light.

The Höchst Farbwerke also prepares special sensitive colours suitable, *inter alia*, for the manufacture of light-filters and for three-colour photography.

The actual inventor of *three-colour printing* was *Christoph le Blonds*, of Paris, who in 1740 patented a process in which the colour effect was obtained by a superimposed printing of the three primary colours, yellow, red, and blue. It was, however, not until photography became popular that e Blonds' invention attained the position warranted by its merits. Orthochromatic photography affords the possibility of reproducing the tone-values and details in the three primary colours, each on a specially sensitised plate, the original being photographed three times from the same point of view, each negative containing a portion of the subject corresponding to one of the three primary colours, yellow, red, and blue. In each photograph two colours operate on the plate, while the third is excluded. This latter process is effected by means of *light-filters*, consisting of sheets of glass or gelatine stained with certain colouring matters. These filters prevent the absorbed rays from acting on the sensitive emulsion of the photographic plates in the camera, so that on development the parts corresponding to the arrested colour rays remain transparent, whilst the silver on the unprotected parts of the plate is more or less reduced. By certain additions the plates are made particularly sensitive for the separate colours—a process invented by *Professor Vogel*, Berlin. A plate which is intended to give the negative for the blue portions of the subject is, for example, made sensitive for red and blue with cyanine, since the light which is to act on these plates must be free from all blue and violet rays, and for this purpose a light-filter absorbing blue and violet is mounted in front (or behind) the lens. This filter is stained with Biebrich scarlet or safranine. The prints obtained from the developed and fixed plates then represent the colour-value of the absorbed rays in the picture, and form the basis of the autotype block, which serves for the printing of these colour-values with the corresponding pigments.

The evolution of the theory and the principle of the three-colour process are also due to Professor Vogel. *Kurtz*, of New York, who purchased the patent, employed the process for autotype printing, and it is now used both for lithographic and block printing in three-colour work, the etched style being less suitable.

Into this subject, however, we cannot go more deeply at present, our purpose being simply to point to the matter as another sphere of application for the products of the colour industry.*

* * *

With regard to *the effect of mixing colours of different properties*, very contradictory opinions are expressed even by practical men and scientific investigators. While some ridicule the alleged effect of colours containing sulphur on lead colours—viz., of ultramarine or vermilion on white lead—others warn us against the use of such mixtures. Probably both parties base their claims on observation; and it may also be admitted that in such cases chemical changes do not necessarily always occur. The more carefully the pigments in question are manufactured—viz., the purer they are—the less will they be liable to undergo the changes in question.

In order to form an independent judgment, the authors have prepared the following mixtures from selected, pure commercial pigments, equal quantities of each ingredient being taken:

1. Vermilion and white lead.
2. Ultramarine and white lead.
3. Chrome yellow and ultramarine.
4. Lithopone and white lead.
5. Lithopone and chrome yellow.

The samples, thoroughly ground together in a mortar, were placed in glasses, one glass of each sample being mixed with water and one with oil. The well-mixed samples were hermetically sealed in the glasses, and attached to a sheet of cardboard hung up in a room, so as to be exposed to diffuse daylight, but not to direct sunshine. The samples were kept well mixed by frequently changing the position of the cardboard.

The observations made with these samples tend to prove that chemical reaction is by no means impossible here. After the lapse of a year the mixture of ultramarine and white lead had kept the best, the vermilion and white lead mixture the worst. The vermilion in both glasses has become dark brown all over. It should be pointed out that a small part of the colour mixture which remained between the cork and the glass, and out of contact with the liquid, has retained its original shade unimpaired. Hence it would appear that the change requires the co-operation of the liquids (oil and water) as well as light. The mixture of ultramarine and white lead exhibits scarcely any change at all, but the other substances experimented with have become visibly discoloured, though not to any great extent. The dry mixtures kept in the dark show no change of tone.

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* Another three-colour process of recent date, that of *Lumière*, employs starch grains stained red, blue, and yellow respectively as an ingredient of the emulsion, the exposed plate furnishing a transparent positive. [TRANSLATOR.]

After these experimental results we cannot agree with those who deny the occurrence of any change.

That organic colouring matters can react chemically on one another has been mentioned already.

The influence of the vehicle on the colours is only of special importance in a few cases. The colour is in most cases mechanically suspended in the vehicle, but it may also be dissolved therein or chemically combined with it. If, for example, we grind ochre or colcothar or vermilion in oil or in a watery vehicle, a mechanical distribution alone is produced. The colour is suspended in its vehicle, and is held firmly in suspension by the latter on drying. If a coal-tar colour be ground in a watery vehicle, it will in most cases dissolve therein, forming a transparent colour such as is used in water-colour painting (*aquarelle*), whereas the colours from the first-named example will be opaque. If a lake precipitated on pure alumina be ground in oil, or white lead and chrome yellow are treated in the same way, a form of chemical combination takes place, the colours and vehicle being saponified, with formation of aluminium and lead soap respectively. This process clearly determines the consistency, covering power, and combining capacity of the colours on the base. Such a close combination of pigment and vehicle will in most cases be advantageous for the purposes to which the colour is to be applied.

If the vehicle be of organic nature and liable to spoil, it may exert a detrimental influence. If, for example, a paste begins to decompose, the organic—and sometimes even inorganic—colours in contact with it may be entirely destroyed. Such a result has often been observed in the case of the colours of wall-papers hung in damp rooms.

APPENDIX

TABLE I.—ATOMIC WEIGHTS AS DETERMINED BY THE GERMAN CHEMICAL SOCIETY.

Element.	Symbol and Valency.	Atomic Weight.	
		O = 16.	H = 1.
*Aluminium	Al$^{iii, iv}$	27·1	27·04
*Antimony	Sb$^{iii, iv}$	120	119·6
*Arsenic	As$^{iii, v}$	75	74·9
*Barium	Ba$^{ii, iv}$	137·4	136·86
*Bismuth	Bi$^{iii, v}$	208·5	207·5
Boron	Bo$^{iii, iv}$	11	10 9
Bromine	Br$^{i, iii, v, vii}$	79·96	79·76
Cadmium	Cd^{ii}	112·4	111·7
Calcium	Ca^{ii}	40	39·91
*Carbon	C$^{ii, iv}$	12	11·97
*Chlorine	Cl$^{i, iii, v, vii}$	35·5	35·37
*Chromium	Cr$^{iii, iv, vi}$	52·1	52·45
*Cobalt	Co$^{ii, iv}$	59	58·6
*Copper	Cu$^{ii, i}$	63·6	63·18
Fluorine	F^{i}	19	19·06
Gold	Au$^{i, iii}$	197·2	196·2
*Hydrogen	H^{i}	1·01	1
*Iodine	I$^{i, iv, v, vii}$	126·85	126·54
*Iron	Fe$^{ii, iii, iv, vi}$	56	55·88
*Lead	Pb$^{ii, iv}$	206·9	206·39
Lithium	Li^{i}	7·03	7·01
Magnesium	Mg^{ii}	24·36	23·94
*Manganese	Mn$^{ii, iv, vi, vii}$	55	54·8
*Mercury	Hg$^{i, ii}$	203	199·8
Molybdenum	Mo$^{ii, iii, iv, vi}$	96	95·9
Nickel	Ni$^{ii, iii, iv}$	58·7	58·6
*Nitrogen	Az (N)$^{iii, v}$	14·04	14·01
*Oxygen	O^{ii}	16	15·96
*Phosphorus	P$^{iii, v}$	31·6	30·96
Platinum	Pt$^{ii, iv, vi}$	194·8	194·34
*Potassium	K^{i}	39·15	39·03
Silicon *	Si^{iv}	28·4	28
*Silver	Ag^{i}	107·93	107·66
*Sodium	Na^{i}	23·05	22·99
Strontium	Sr^{ii}	87·6	87·3
*Sulphur	S$^{ii, iv, vi, viii}$	32·06	31·98
*Tin	Sn$^{ii, iv}$	118·5	117·35
Tungsten (Wolfram)	W$^{iv, vi}$	184	183·6
*Zinc	Zn^{ii}	65·4	64·88

TABLE II.—SOLUBILITY

Abbreviations: s., soluble; r.s., readily soluble; s.s., sparingly soluble; i., insoluble; decomp., decomposed.

Name.	Formula.	Molecular Weight.	Solubility in 100 Parts of Water.	
			Cold.	Hot.
Alum (ammonium)	$Al_2(SO_4)_3(NH_4)_2SO_4 + 24H_2O$	904·4	9	422
„ (potassium)	$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O$	948	9·5	357
„ (sodium)	$Al(SO_4)_3 + Na_2SO_4 + 24H_2O$	917	110	r.s.
Aluminium chloride	$Al_2Cl_6(+12H_2O)$	265·8	400	—
„ hydroxide (alumina)	$Al_2(OH)_6$	155·8	i.	i.
„ nitrate	$Al_2(NO_3)_6 + 15H_2O$	694·7	Liquefies	—
„ phosphate	$Al_2(PO_4)_2$	244	i.	i.
„ sulphate	$Al_2(SO_4)_3 + 18H_2O$	664·8	85	1130
Ammonia	NH_3	17	105	97 vol. on 100°
Ammonium carbonate, norm.	$(NH_4)_2CO_3 + H_2O$	114	r.s.	r.s.
Ammonium carbonate, prim.	$(NH_4)HCO_3$	79	25	Decomp.
Ammonium chloride (sal ammon.)	NH_4Cl	53·38	33 parts at 10°	73 parts at 100°
„ phosphate (dry)	$(NH_4)_2HPO_4$	132	25	r.s.
„ sulphate	$(NH_4)_2SO_4$	132	76	98
Antimony chloride	$SbCl_3$	225·7	r.s.	Decomp.
„ pentasulphide	Sb_2S_5	399	i.	i.
„ trisulphide	Sb_2S_3	335	i.	i.
Antimonic acid	$HSbO_3$	168·5	s.s.	s.s.
Antimonious acid	$HSbO_2$	152·5	i.	i.
Arsenic	As_2O_3	198	4	9·5
„ disulphide	As_2S_2	214	i.	i.
„ trisulphide	As_2S_3	245·2	i.	i.
Barium carbonate	$BaCO_3$	197	i.	i.
„ chloride	$BaCl_2 + 2H_2O$	244	33·4 parts at 10°	60 parts at 100°
„ chromate	$BaCrO_4$	253	s.s.	s.s.
„ sulphate	$BaSO_4$	232·7	i.	i.
„ sulphide	BaS	169	Decomp.	Decomp.
Bleaching powder	$CaOCl_2$	127	s.s.	—
Boric acid	H_3BO_3	62	4	34
Cadmium carbonate	$CdCO_4$	172	i.	i.
„ chloride	$CdCl_2 + 2H_2O$	219	140	150
„ nitrate	$Cd(NO_3)_2 + 4H_2O$	307·3	Liquefies	—
„ oxide	CdO	128	i.	i.
„ sulphate	$CdSO_4 + 4H_2O$	280	95	r.s.
„ sulphide	CdS	144	i.	i.
Calcium carbide	CaC_2	64	Decomp.	Decomp.
„ carbonate (chalk)	$CaCO_3$	100	s.s.	s.s.
„ chloride	$CaCl_2 + 6H_2O$	219	64 parts at 10°	120 parts at 100°
„ hydroxide	$Ca(OH)_2$	74	0·14 part at 10°	0·075 part at 100°
„ metaphosphate	$Ca(PO_3)_2$	198	i.	i.
„ phosphate, prim.	$CaH_4(PO_4)_2 + H_2O$	252	Decomp.	Decomp.
„ „ sec.	$CaHPO_4 + 2H_2O$	172	i.	i.
„ „ tert.	$Ca_3(PO_4)_2$	310	i.	—
„ sulphate	$CaSO_4 + 2H_2O$	172	0·2 part at 0°	0·21 part in 100°

TABLE II.—*continued*

Name.	Formula.	Molecular Weight.	Solubility in 100 Parts of Water.	
			Cold.	Hot.
Carbon dioxide . .	CO_2	44	—	—
„ disulphide. .	CS_2	76	0·2 parts at 0°	1·4 : 10,000 at 50°
Chromium chloride .	$CrCl_3$	123·2	s.	s.
„ hydroxide .	$Cr_2(OH)_6+4H_2O$	279	i.	i.
„ oxide . .	Cr_2O_3	153	i.	i.
„ sulphate .	$Cr_2(SO_4)_3+18H_2O$	717	s.	s.
Copper acetate (verdigris) . .	$Cu(C_2H_3O_2)_2+H_2O$	199	1	20
„ carbonate (malachite) . .	$CuCO_3+Cu(OH)_2$	221	i.	i.
„ carbonate (mountain blue) .	$2(CuCO_3)+Cu(OH)_2$	344	i.	i.
„ sulphate . .	$CuSO_4+5H_2O$	249·5	40	203
Hydrochloric acid . .	HCl	36·4	525 : 1 v.	—
Iron dichloride (ferrous chloride) . .	$FeCl_2+4H_2O$	199	130	r.s.
„ hydroxide (ferric) .	$Fe_2(OH)_6$	214	i.	i.
„ oxide (hematite) (ferric) .	Fe_2O_3	160	i.	i.
„ (ferrous) .	FeO	72	i.	i.
„ perchloride (ferric chloride) . .	Fe_2Cl_6	325	Liquefies	—
„ protohydroxide (ferrous) . . .	$Fe(OH)_2$	90	i.	i.
„ sulphate (ferric) .	$Fe(SO_4)_3+9H_2O$	562	r.s.	Liquefies
„ „ (ferrous) .	$FeSO_4+7H_2O$	278	60	333
Lead acetate, neutr. .	$Pb(C_2H_3O_2)_2$	—	r.s.	r.s.
„ carbonate, neutr. .	$PbCO_3$	266	i.	i.
„ „ bas. (white lead) .	$2PbCO_3,Pb(OH)_2$	772·9	i.	i.
„ chloride . .	$PbCl_2$	277	0·74	5
„ chromate ("chromes") .	$PbCrO_4$	323	i.	i.
„ hydroxide . .	$Pb(OH)_2$	241	s.s.	s.s.
„ nitrate . . .	$Pb(NO_3)_2$	330	48 parts at 10°	139 parts at 100°
„ oxide . . .	PbO	222·4	i.	i.
„ phosphate . .	$Pb_3(PO_4)_2$	808·8	—	—
„ sesquioxide (red lead) . . .	Pb_2O_3	460·7	i.	i.
„ sulphate, neutr. .	$PbSO_4$	302	s.s.	s.
„ „ bas. .	$PbSO_4,PbO$	524·7	s.s.	s.
Magnesium carbonate .	$MgCO_3$	84	i.	i.
„ chloride .	$MgCl_2+6H_2O$	203·3	130	367
Mercury sulphide (vermilion) . . .	HgS	232	i.	i.
Nitric acid . . .	HNO_3	63	∞	∞
Potassium bichromate .	$K_2Cr_2O_7$	295	12·4 parts at 20°	94
„ carbonate (potash) .	$K_2CO_3+2H_2O$	174	r.s.	r.s.
„ chlorate (Bertholet's salt)	$KClO_3$	122·5	6·5	50
„ chloride .	KCl	74·5	32	57

TABLE II.—*continued*

Name.	Formula.	Molecular Weight.	Solubility in 100 Parts of Water.	
			Cold.	Hot.
Potassium nitrate (saltpetre) . .	KNO_3	101	25	200
,, permanganate	$KMnO_4$	158	6·5	r.s.
,, sulphate .	K_2SO_4	174	12·5	25
Sodium acetate . .	$NaC_2H_3O_2+3H_2O$	136	33	200
,, aluminate . .	$Na_2Al_2O_4$	164	r.s.	r.s.
,, bichromate .	$Na_2Cr_2O_7+2H_2O$	299	Liquefies	—
,, borate (borax) .	$Na_2B_4O_7+10H_2O$	382	6	200
,, carbonate (soda, cryst.) . .	$Na_2CO_3+10H_2O$	286	21	420
,, carbonate (soda, calc.) . .	Na_2CO_3	106	7	45
,, chloride (common salt) .	$NaCl$	58·5	35	38
,, chromate . .	$Na_2CrO_4+10H_2O$	342·5	r.s.	r.s.
,, hydroxide (caustic soda) .	$NaOH$	40	60	210
,, hydrosulphide .	$NaHS+2H_2O$	92	Liquefies	—
,, nitrate (soda, saltpetre) .	$NaNO_3$	85	80	200
,, nitrite ("nitrite") . .	$NaNO_2$	69	r.s.	r.s.
,, phosphate, meta-	$NaPO_4$	102	i.	i.
,, ,, norm	$Na_3PO_4+12H_2O$	380	20	r.s.
,, ,, prim.	$NaH_2PO_4+4H_2O$	191·7	1	—
,, ,, sec. .	$Na_2HPO_4+12H_2O$	358	3	96
,, pyrophosphate .	$Na_4P_2O_7+10H_2O$	446	10	93
,, silicate . .	Na_2SiO_3	122·5	s.	s.
,, ,, (silicate of soda)	Na_2SiO_9	303·6	s.	s.
,, sulphate (Glauber salt) . .	$Na_2SO_4+10H_2O$	322	5 parts at 0°	42·5
,, sulphide . .	$Na_2S(+9H_2O)$	240	s.	s.
Sulphuretted hydrogen .	SH_2	34	1 : 1·37 v. 0°	3·23 v. 15°
Sulphuric acid, conc. .	H_2SO_4	98	∞	∞
,, ,, fuming .	$H_2S_2O_7$	178	Decomp.	Decomp.
Tannic acid (digallic acid)	$C_{14}H_{10}O_9$	322	Pure, r.s.	Pure, r.s.
Tin chloride . . .	$SnCl_2+2H_2O$	225	271	Decomp. with much water
,, tetrachloride . .	$SnCl_4$	260	Decomp. with much water	id.
Water	H_2O	18	—	—
Zinc acetate . . .	$Zn(C_2H_3O_2)_2+3H_2O$	237	r.s.	r.s.
,, carbonate . .	$ZnCO_3+7H_2O$	143	i.	i.
,, chloride . .	$ZnCl_2$	136	300	r.s.
,, hydroxide . .	$Zn(OH)_2$	99	i.	i.
,, oxide (zinc white) .	ZnO	81	s.s.	—
,, sulphate. . .	$ZnSO_4+7H_2O$	287	135	655
,, sulphide (component of lithopone) .	ZnS	97	i.	i.

TABLE III.—VOLUME WEIGHT OF CAUSTIC SODA AT 15° C. (LUNGE)

Specific Weight.	Degree B.	NaOH per Cent.	Specific Weight.	Degree B.	NaOH per Cent.
1·007	1	0·61	1·220	26	19·58
1·014	2	1·20	1·231	27	20·59
1·022	3	2·00	1·241	28	21·42
1·029	4	2·71	1·252	29	22·64
1·036	5	3·35	1·263	30	23·67
1·045	6	4·00	1·274	31	24·81
1·052	8	4·64	1·285	32	25·80
1·060	7	5·29	1·297	33	26·83
1 067	9	5·87	1·308	34	27·80
1·075	10	6·55	1·320	35	28·83
1·083	11	7·31	1·332	36	29·93
1·091	12	8·00	1·345	37	31·22
1·100	13	8·68	1·357	38	32·47
1·108	14	9·42	1·370	39	33·69
1·116	15	10·06	1·383	40	34·96
1·125	16	10·97	1·397	41	36·25
1·134	17	11·84	1·410	42	37·47
1·142	18	12·64	1·424	43	38 80
1·152	19	13·55	1·438	44	39·99
1·162	20	14·37	1·453	45	41·41
1·171	21	15·13	1·468	46	42·83
1·180	22	15·91	1·483	47	44·38
1·190	23	16·77	1·498	48	46·15
1·200	24	17·67	1·514	49	47·60
1·210	25	18·58	1·530	50	49·02

Note on Table III.—Assuming that 23 kg. of dry caustic soda (NaOH) are required to precipitate completely a given quantity of copper sulphate, and that a solution of the former of unknown strength is at disposal, how much of this solution corresponds to the 23 kg. of dry caustic soda required? Supposing the solution is of 33° B. strength, then, according to the above table, it will contain 26·83 parts of dry caustic soda per 100 parts. From this the quantity of solution corresponding to 23 kg. of dry caustic soda can be calculated according to the equation 26·8 : 100 = 23 : x.

$$x = \frac{23 : 100}{26{\cdot}8} = 85{\cdot}8 \text{ kg. of caustic soda.}$$

If an areometer is not at disposal the same result is obtainable by means of the specific gravity. For this purpose an accurately weighed small glass bottle containing 100 c.c. when filled up to the mark is filled with the caustic soda in question, and the weight of this solution is ascertained. If the liquid (less tare) weighs 129·7 grms., then the specific gravity of the liquid is 129·7 divided by the number of cubic centimetres, or in our case

$$\frac{129{\cdot}7}{100} = 1{\cdot}297.$$

By the aid of Table III. we find that a caustic soda solution of this specific weight contains 26·83 parts by weight per 100 parts, and corresponds exactly to 33° B.

TABLE IV.—SPECIFIC GRAVITY AND PERCENTAGE CONTENT OF SODA SOLUTIONS AT 15° C. (LUNGE)

Specific Gravity.	Degrees B.	Percentage Weight.	
		Soda, Calcined.	Soda, Crystals.
1·007	1	0·67	1·807
1·014	2	1·33	3·587
1·022	3	2·09	5·637
1·029	4	2·76	7·444
1·036	5	3·43	9·251
1·045	6	4·29	11·570
1·052	7	4·94	13·323
1·060	8	5·71	15·400
1·067	9	6·37	17·180
1·075	10	7·12	19·203
1·083	11	7·88	21·252
1·091	12	8·62	23·248
1·100	13	9·43	25·432
1·108	14	10·19	27·482
1·116	15	10·95	29·532
1·125	16	11·81	31·851
1·134	17	12·61	34·009
1·142	18	13·16	35·493
1·152	19	14·24	38·405

TABLE V.—SPECIFIC GRAVITY AND PERCENTAGE CONTENT OF GLAUBER SALT SOLUTIONS AT 19° C. (SCHIFF)

Specific Gravity.	Percentage.		Specific Gravity.	Percentage.		Specific Gravity.	Percentage.	
	Calcined Glauber Salt.	Crystallised Glauber Salt.		Calcined Glauber Salt.	Crystallised Glauber Salt.		Calcined Glauber Salt.	Crystallised Glauber Salt.
1·0040	0·441	1	1·0439	4·851	11	1·0849	9·261	21
1·0079	0·881	2	1·0479	5·292	12	1·0890	9·702	22
1·0118	1·323	3	1·0520	5·673	13	1·0931	10·143	23
1·0158	1·764	4	1·0560	6·174	14	1·0973	10·584	24
1·0198	2·205	5	1·0601	6·615	15	1·1015	11·025	25
1·0238	2·646	6	1·0642	7·056	16	1·1057	11·466	26
1·0278	3·087	7	1·0683	7·497	17	1·1100	11·907	27
1·0318	3·528	8	1·0725	7·938	18	1·1142	12·348	28
1·0358	3·969	9	1·0766	8·379	19	1·1184	12·789	29
1·0398	4·410	10	1·0807	8·820	20	1·1236	13·220	30

Table VI.—SPECIFIC GRAVITY AND PERCENTAGE CONTENT OF SOLUTIONS OF ALUMINIUM SULPHATE AT 15° C.

Specific Gravity.	$Al_2(SO_4)_3$ per Cent.	Specific Gravity.	$Al_2(SO_4)_3$ per Cent.	Specific Gravity.	$Al_2(SO_4)_3$ per Cent.	Specific Gravity.	$Al_2(SO_4)_3$ per Cent.
1·0170	1	1·0870	8	1·1467	14	1·2074	20
1·0270	2	1·0968	9	1·1574	15	1·2168	21
1·0370	3	1·1071	10	1·1668	16	1·2274	22
1·0470	4	1·1171	11	1·1770	17	1·2375	23
1·0569	5	1·1270	12	1·1876	18	1·2473	24
1·0670	6	1·1369	13	1·1971	19	1·2573	25
1·0768	7						

Table VII.—SPECIFIC GRAVITY AND PERCENTAGE CONTENT OF SOLUTIONS OF ZINC SULPHATE AT 15° C. (GERLACH)

Specific Gravity.	$ZnSO_4$ per Cent.	$ZnSO_4 + 7H_2O$ per Cent.	Specific Gravity.	$ZnSO_4$ per Cent.	$ZnSO_4$ + 7Aq. per Cent.
1·0288	2·805	5	1·2315	19·637	35
1·0593	5·611	10	1·2709	22·443	40
1·0905	8·416	15	1·3100	25·248	45
1·1236	11·220	20	1·3532	28·054	50
1·1574	14·027	25	1·3986	30·859	55
1·1933	16·832	30	1·4451	33·664	60

Table VIII.—SPECIFIC GRAVITY AND PERCENTAGE CONTENT OF ZINC CHLORIDE SOLUTIONS AT 19 5° C.

Specific Gravity.	$ZnCl_2$ per Cent.	Specific Gravity.	$ZnCl_2$ per Cent.	Specific Gravity.	$ZnCl_2$ per Cent.	Specific Gravity.	$ZnCl_2$ per Cent.
1·045	5	1·186	20	1·352	35	1·566	50
1·091	10	1·238	25	1·420	40	1·650	55
1·137	15	1 291	30	1·488	45	1·740	60

TABLE IX.—SPECIFIC GRAVITY AND PERCENTAGE CONTENT OF SOLUTIONS OF COPPER SULPHATE AT 17° C.

Specific Gravity.	$CuSO_4$ 5Aq. per Cent.	Specific Gravity.	$CuSO_4$ 5Aq. per Cent.	Specific Gravity.	$CuSO_4$ 5Aq. per Cent.	Specific Gravity.	$CuSO_4$ 5Aq. per Cent.
1·0126	2	1·0516	8	1·0933	14	1·1354	20
1·0254	4	1·0649	10	1·1063	16	1·1501	22
1·0384	6	1·0785	12	1·1208	18	1·1659	24

TABLE X.—SPECIFIC GRAVITY AND PERCENTAGE CONTENT OF SOLUTIONS OF FERROUS SULPHATE AT 15° C.

Specific Gravity.	$FeSO_4$ + 7Aq per Cent.	Specific Gravity.	$FeSO_4$ + 7Aq per Cent.	Specific Gravity.	$FeSO_4$ + 7Aq. per Cent.	Specific Gravity.	$FeSO_4$ + 7Aq. per Cent.
1·011	2	1·043	8	1·082	15	1·174	30
1·021	4	1·054	10	1·112	20	1·206	35
1·032	6	1·065	12	1·143	25	1·239	40

TABLE XI.—SPECIFIC GRAVITY AND PERCENTAGE CONTENT OF BARIUM CHLORIDE SOLUTIONS AT 21·5° C.

Specific Gravity.	$BaCl_2 + 2H_2O$ per Cent.	Specific Gravity.	$BaCl_2 + 2H_2O$ per Cent.
1·0073	1	1·1302	16
1·0147	2	1·1394	17
1·0222	3	1·1488	18
1·0298	4	1·1584	19
1·0374	5	1·1683	20
1·0452	6	1·1783	21
1·0530	7	1·1884	22
1·0610	8	1·1986	23
1·0692	9	1·2090	24
1·0776	10	1·2197	25
1·0861	11	1·2304	26
1·0947	12	1·2413	27
1·1034	13	1·2523	28
1·1122	14	1·2636	29
1·1211	15	1·2750	30

TABLE XII.—SPECIFIC GRAVITY AND PERCENTAGE CONTENT OF LEAD ACETATE SOLUTIONS AT 20° C. (F. SALOMON)

Grms. in 100 c.c.	Specific Gravity.	Grms. in 100 c.c.	Specific Gravity.	Grms. in 100 c.c.	Specific Gravity.	Grms. in 100 c.c.	Specific Gravity.
1	1·0062	14	1·0870	27	1·1663	40	1·2440
2	1·0124	15	1·0932	28	1·1723	41	1·2499
3	1·0186	16	1·0994	29	1·1783	42	1·2558
4	1·0248	17	1·1056	30	1·1844	43	1·2617
5	1·0311	18	1·1118	31	1·1903	44	1·2676
6	1·0373	19	1·1180	32	1·1963	45	1·2735
7	1·0435	20	1·1242	33	1·2022	46	1·2794
8	1·0497	21	1·1302	34	1·2082	47	1·2853
9	1·0559	22	1·1362	35	1·2142	48	1·2912
10	1·0622	23	1·1422	36	1·2201	49	1·2971
11	1·0684	24	1·1482	37	1·2261	50	1·3030
12	1·0746	25	1·1543	38	1·2320		
13	1·0808	26	1·1603	39	1·2380		

TABLE XIII.—SPECIFIC GRAVITY OF HYDROCHLORIC ACID (LUNGE AND MARCHLEWSKY)

Specific Gravity at $\frac{15°}{4°}$ (*in vacuo*).	Degrees B.	Percentage Contents of		1 Litre contains Kg.	
		HCl.	Acid 20° B.	HCl.	Acid 20° B.
1·000	0·0	0·16	0·49	0·0016	0·0049
1·005	0·7	1·15	3·58	0·012	0·036
1·010	1·4	2·14	6·66	0·022	0·067
1·015	2·1	3·12	9·71	0·032	0·099
1·020	2·7	4·13	12·86	0·042	0·131
1·025	3·4	5·15	16·04	0·053	0·164
1·030	4·1	6·15	19·16	0·064	0·197
1·035	4·7	7·15	22·27	0·074	0·231
1·040	5·4	8·16	25·42	0·085	0·264
1·045	6·0	9·16	28·53	0·096	0·298
1·050	6·7	10·17	31·68	0·107	0·333
1·055	7·4	11·18	34·82	0·118	0·367
1·060	8·0	12·19	37·97	0·129	0·403
1·065	8·7	13·19	41·09	0·141	0·438
1·070	9·4	14·17	44·14	0·152	0·472
1·075	10·0	15·16	47·22	0·163	0·508
1·080	10·6	16·15	50·31	0·174	0·543
1·085	11·2	17·13	53·36	0·186	0·579
1·090	11·9	18·11	56·41	0·197	0·615
1·095	12·4	19·06	59·37	0·209	0·650
1·100	13·0	20·01	62·33	0·220	0·686
1·105	13·6	20·97	65·32	0·232	0·722
1·110	14·2	21·92	68·28	0·243	0·758
1·115	14·9	22·86	71·21	0·255	0·794
1·120	15·4	23·82	74·20	0·267	0·831
1·125	16·0	24·78	77·19	0·278	0·868

TABLE XIII.—*continued*

Specific Gravity at $\frac{15^\circ}{4^\circ}$ (*in vacuo*).	Degrees B.	Percentage Content of		1 Litre contains Kg.	
		HCl.	Acid 20° B.	HCl.	Acid 20° B.
1·130	16·5	25·75	80·21	0·291	0·906
1·135	17·1	26·70	83·18	0·303	0·944
1·140	17·7	27·66	86·17	0·315	0·982
1·142	18·0	28·14	87·66	0·322	1·002
1·145	18·3	28·61	89·13	0·328	1·021
1·150	18·8	29·57	92·11	0·340	1·059
1·152	19·0	29·95	93·30	0·345	1·075
1·155	19·3	30·55	95·17	0·353	1·099
1·160	19·8	31·52	98·19	0·366	1·139
1·1627	20·0	32·10	100·00	0·373	1·163
1·165	20·3	32·49	101·21	0·379	1·179
1·170	20·9	33·46	104·24	0·392	1·220
1·171	21·0	33·65	104·82	0·394	1·227
1·175	21·4	34·42	107·22	0·404	1·260
1·180	22·0	35·39	110·24	0·418	1·301
1·185	22·5	36·31	113·11	0·430	1·340
1·190	23·0	37·23	115·98	0·443	1·380
1·195	23·5	38·16	118·87	0·456	1·421
1·200	24·0	39·11	121·84	0·469	1·462

TABLE XIV.—SPECIFIC GRAVITY OF NITRIC ACID AT 15° C.

Specific Gravity.	Degrees B.	100 Parts contain grms. HNO_3.	Specific Gravity.	Degrees B.	100 Parts contain grms. HNO_3.
1·007	1	1·5	1·231	27	37·0
1·014	2	2·6	1·242	28	38·6
1·022	3	4·0	1·252	29	40·2
1·029	4	5·1	1·261	30	41·5
1·036	5	6·3	1·275	31	43·5
1·044	6	7·6	1·286	32	45·0
1·052	7	9·0	1·298	33	47·1
1·060	8	10·2	1·309	34	48·6
1·067	9	11·4	1·321	35	50·7
1·075	10	12·7	1·334	36	52·9
1·083	11	14·0	1·346	37	55·0
1·091	12	15·3	1·359	38	57·3
1·100	13	16·8	1·372	39	59·6
1·108	14	18·0	1·384	40	61·7
1·116	15	19·4	1·398	41	64·5
1·125	16	20·8	1·412	42	67·5
1·134	17	22·2	1·426	43	70·6
1·143	18	23·6	1·440	44	74·4
1·152	19	24·9	1·454	45	78·4
1·161	20	26·3	1·470	46	83·0
1·171	21	27·8	1·485	47	87·1
1·180	22	29·2	1·501	48	92·6
1·190	23	30·7	1·516	49	96·0
1·199	24	32·1	1·524	49·5	98·0
1·210	25	33·8	1·530	49·9	100·0
1 221	26	35·5			

TABLE XV.—SPECIFIC GRAVITY OF SULPHURIC ACID AT 15° C.

Specific Gravity.	Degrees B.	Percentage of pure H_2SO_4.	Content of H_2SO_4 in Kgs. per Litre.	Specific Gravity.	Degrees B.	Percentage of pure H_2SO_4.	Content of H_2SO_4 in Kgs. per Litre.
1·01	1·4	1·57	0·016	1·47	41·1	56·90	0·837
1·02	2·7	3·03	0·031	1·48	46·8	57·83	0·856
1·03	4·1	4·49	0·046	1·49	47·4	58·74	0·876
1·04	5·4	5·96	0·062	1·50	48·1	59·70	0·896
1·05	6·7	7·37	0·077	1·51	48·7	60·65	0·916
1·06	8·0	8·77	0·093	1·52	49·4	61·59	0·936
1·07	9·4	10·19	0·109	1·53	50·0	62·53	0·957
1·08	10·6	11·60	0·125	1·54	50·6	63·43	0·977
1·09	11·9	12·99	0·142	1·55	51·2	64·26	0·996
1·10	13·0	14·35	0·158	1·56	51·8	65·08	1·015
1·11	14·2	15·71	0·175	1·57	52·4	65·90	1·025
1·12	15·4	17·01	0·191	1·58	53·0	66·71	1·054
1·13	16·5	18·31	0·207	1·59	53·6	67·59	1·075
1·14	17·7	19·61	0·223	1·60	54·1	68·51	1·096
1·15	18·8	20·91	0·239	1·61	54·7	69·43	1·118
1·16	19·8	22·19	0·257	1·62	55·2	70·32	1·139
1·17	20·9	23·47	0·275	1·63	55·8	71·16	1·160
1·18	22·0	24·76	0·292	1·64	56·3	71·99	1·181
1·19	23·0	26·04	0·310	1·65	56·9	72·82	1·202
1·20	24·0	27·32	0·328	1·66	57·4	73·64	1·222
1·21	25·0	28·58	0·346	1·67	57·9	74·51	1·244
1·22	26·0	29·84	0·364	1·68	58·4	75·42	1·267
1·23	26·9	31·11	0·382	1·69	58·9	76·30	1·289
1·24	27·9	32·28	0·400	1·70	59·5	77·17	1·312
1·25	28·8	33·43	0·418	1·71	60·0	78·04	1·334
1·26	29·7	34·57	0·435	1·72	60·4	78·92	1·357
1·27	30·6	35·71	0·454	1·73	60·9	79·80	1·381
1·28	31·5	36·87	0·472	1·74	61·4	80·68	1·404
1·29	32·4	38·03	0·490	1·75	61·8	81·56	1·427
1·30	33·3	39·19	0·510	1·76	62·3	82·44	1·451
1·31	34·2	40·35	0·529	1·77	62·8	83·32	1·475
1·32	35·0	41·50	0·548	1·78	63·2	84·50	1·504
1·33	35·8	42·66	0·567	1·79	63·7	85·70	1·534
1·34	36·6	43·74	0·586	1·80	64·2	86·90	1·564
1·35	37·4	44·82	0·605	1·81	64·6	88·30	1·598
1·36	38·2	45·88	0·624	1·82	65·0	90·05	1·639
1·37	39·0	46·94	0·643	1·822	65·1	90·40	1·647
1·38	39·8	48·00	0·662	1·824	65·2	90·80	1·656
1·39	40·5	49·06	0·682	1·826	65·3	91·25	1·666
1·40	41·2	50·11	0·702	1·828	65·4	91·70	1·676
1·41	42·0	51·15	0·721	1·831	65·5	92·30	1·690
1·42	42·7	52·15	0·740	1·833	65·6	92·75	1·700
1·43	43·4	53·11	0·759	1·835	65·7	93·43	1·713
1·44	44·1	54·07	0·779	1·838	65·8	94·60	1·739
1·45	44·8	55·03	0·798	1·840	65·9	95·60	1·759
1·46	45·4	55·97	0·817				

TABLE XVI.—SPECIFIC GRAVITY OF FERRIC CHLORIDE (FRANZ).

Specific Gravity.	Fe_2Cl_6 per Cent.	Specific Gravity.	Fe_2Cl_6 per Cent.	Specific Gravity.	Fe_2Cl_6 per Cent.
1·015	2	1·175	22	1·387	42
1·029	4	1·195	24	1·412	44
1·044	6	1·216	26	1·437	46
1·059	8	1·237	28	1·462	48
1·073	10	1·257	30	1·487	50
1·089	12	1 278	32	1·515	52
1·105	14	1·299	34	1·544	54
1·122	16	1·320	36	1·573	56
1·138	18	1·341	38	1·602	58
1·159	20	1·362	40	1·632	60

USE OF THE ACID TABLES

Example.—10 kg. sulphuric acid, 66° B. are required, and an acid of 52° B. strength is at disposal. What quantity of this latter will correspond to the required weight?

By the aid of Table XV. we find that 10 kg. of sulphuric acid, 66° B. (65·9), contain 9·56 kg. of pure acid. According to the table, 10 kg. sulphuric acid, 52° B., would correspond to 6·508 of pure sulphuric acid. In order to obtain the 9·56 kg., therefore, the quantity needed is found by the following equation:

$$6{\cdot}508 : 9{\cdot}560 = 10 : x \text{ ; or } x = \frac{9{\cdot}56 \times 10}{6{\cdot}508} = \frac{95{\cdot}6}{6{\cdot}51} = 14{\cdot}5 \text{ kg. of } H_2SO_4 \text{ (52° B.).}$$